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Photochemical behaviour of poly(ethylene oxide) (PEO) in aqueous solution: Influence of iron salts

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Abstract

The degradation of poly(ethylene oxide) (PEO) photoinduced ($\lambda \geq 300$ nm) by Fe(III) (6.0×10^{-4} mol L^{-1}) in aqueous solution in the presence of oxygen at 15 °C has been investigated in various experimental conditions of pH and concentrations: pH 3.1 and 7.8 and at three different concentrations of PEO: 0.1, 5.0 and 50.0 g L^{-1}. The formation of oxidation products was followed by infrared analysis of deposit obtained by evaporation of aliquots of irradiated polymer solutions. The photooxidation of PEO aqueous solutions both in the presence and in the absence of Fe(III) leads to the formation of macromolecular formates and esters. Formate ions are formed by the hydrolysis of macromolecular formates leading to the acidification of the medium. The presence of Fe(III) modifies the rate of oxidation especially in weakly acidic medium. The photogenerated $^\bullet$OH radicals from iron species accelerate the oxidation of PEO. Thermooxidation experiments of PEO in aqueous solution in the presence of Fe(III) at 50 °C are also reported and compared with photooxidation results.

Keywords: Poly(ethylene oxide) (PEO); Iron; Photodegradation; Aqueous solution; Mineralisation

1. Introduction

PEO is widely used in many applications such as detergents, paints, drug delivery, etc. At the end of its useful life, it is generally discarded into the aqueous environment simply because it is unrecoverable. This polymer is not biodegradable and its fate in the environment is not well known in terms of PEO concentration really present, degradation and toxicity. Moreover, the potential pollution from this polymer is not visible. Consequently it has received less attention in the media than packaging plastics which visibly litter the countryside and contribute to landfill overland.

A previous paper reported a study carried out to understand the photooxidation ($\lambda \geq 300$ nm) and the thermooxidation at 50 °C of poly(ethylene oxide) (PEO) in the solid state [1]. It was concluded that the mechanism of photodegradation of PEO in the solid state mainly led to the formation of macromolecular formates and esters. Similar studies were carried out in aqueous solution [2,3] in presence of oxygen at 15 °C at different pH's (2.3, 3.1, 7.8, 8.4 and 12.0) and at different PEO concentrations. It has been shown that the photodegradation of PEO in aqueous solution, beside formation of macromolecular formates and esters, results in the formation of formate ions or formic acid depending on the pH of the medium. This product comes from a partial hydrolysis in aqueous solution of formate end groups in the polymer matrix. This process of hydrolysis contributes to the acidification of the medium.

The main objective of the present work is to study the influence of Fe(III) salt, which is a transition metal and an efficient photochemical source of hydoxyl radicals, on the photochemical and thermal degradation of PEO in aqueous solution. The photochemical degradation of PEO in the solid state in presence of oxygen with the introduction of transition metal ions ($FeCl_3, NiCl_2, CoCl_2$ and $CuCl_2$) into polymers has been investigated [4–8]. It was concluded that the photostability of PEO was dramatically reduced in the presence of metal ions and a significant formation of carbonyl, carboxyl and hydroxy/hydroperoxy groups was observed.

The hydrolysis of Fe(III) is a complex phenomenon and a number of equilibria yield numerous species [9]. Previous works have shown that the hydrolysis depends mainly on pH, initial concentration of Fe(III), temperature, ionic strength and

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nature of anions [10]. These different species have distinct chemical reactivity and behaviour under irradiation in aqueous solution. Among the Fe(III) aquacomplexes, $Fe(OH)^{2+}$ (or $[Fe(H_2O)_5(OH)]^{2+}$) is the most photoreactive in terms of hydroxyl radical formation [11] and is the dominant species in moderately acidic solutions (pH 2.5–5.0) [9].

Photoexcitation of $Fe(OH)^{2+}$ forms $^{\bullet}OH$ radicals following ligand-to-metal charge transfer excitation (reaction 1). These radicals are considered to be the oxidant species which are capable to react with most organic compounds.

$$\mathrm{Fe(III)} \xrightarrow[H_2O]{h\nu} \mathrm{Fe(II)} + {}^{\bullet}\mathrm{OH} + \mathrm{H}^+ \qquad (1)$$

The present article reports a study of the degradation of PEO photoinduced by Fe(III) aquacomplexes until its complete mineralisation. The role of Fe(III) species is identified and a mechanism of PEO degradation is proposed. The influence of the pH of the aqueous solution is also studied by comparing the photo- and thermo-degradation of PEO at two pH's 3.1 and 7.8.

2. Experimental

2.1. Materials

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

Poly(ethylene oxide) was obtained from Scientific Polymer Products and used without further purification. The average molecular weight of the polymer was 100,000. Ferric perchlorate nonahydrate ($Fe(ClO_4)_3, 9H_2O$; >97%) was a Fluka product kept in a dessicator. Water was purified by a Millipore Ultra-Pure System ($\rho = 18.2\,M\Omega\,cm$). Irradiations of PEO in solid state (as films) were carried out in a SEPAP 14/24 unit. This apparatus has been designed for the study of polymer photodegradation in artificial ageing corresponding to medium accelerated conditions [12]. The irradiation of PEO aqueous solutions was carried out in an elliptic chamber which is equipped with one medium-pressure mercury lamp (Mazda MA 400, polychromatic emission with an intensity of $22\,W\,m^{-2}$) in a vertical position at one focal axis of the chamber. A glass envelope filters wavelengths below 300 nm. The aqueous solution of PEO was irradiated in a pyrex reactor cooled by water circulation. The temperature of the solution was maintained at 15 °C in order to avoid water evaporation. This reactor was placed at the second focal axis of the chamber. The solutions were continuously stirred with a magnetic stirrer and a Teflon bar.

Thermooxidation experiments were carried out at 50 °C in a 100 mL round bottled flask equipped with reflux condenser. This temperature was chosen to keep the aqueous solution at a temperature below cloud point temperature (CPT = 100 °C). The reactor was therefore placed into an oil bath.

PEO solutions of 5.0% ($50.0\,g\,L^{-1}$), 0.5% ($5.0\,g\,L^{-1}$) and 0.01% ($0.1\,g\,L^{-1}$) of wt.% were prepared by dissolving PEO into distilled and deionized water with mild stirring overnight at room temperature. The aqueous solutions of PEO are not completely homogeneous and that can lead to high TOC variations (cf. Fig. 6a). This polymer has tendency to agglomerate (formation of soluble aggregate) in aqueous solution.

To reach the total dissolution of iron, PEO aqueous solution was first acidified to obtain a pH of 3.5 or 4.0 with $HClO_4$. $Fe(ClO_4)_3$ was dissolved in these PEO solutions at the concentration of $6 \times 10^{-4}\,mol\,L^{-1}$ and $1.2 \times 10^{-3}\,mol\,L^{-1}$, respectively. After iron addition, the pH of the solutions decreased from 3.5 to 3.1. In order to test the influence of the pH, Fe(III) has been dissolved in PEO aqueous solution without further acidification. In these conditions the pH of the solution changed from 8.4 to 7.8 after the addition of $Fe(ClO_4)_3$ ($6 \times 10^{-4}\,mol\,L^{-1}$).

Relatively concentrated solutions of PEO (5.0 and 0.5%) had to be used in order to follow the chemical modifications of the irradiated solutions by IR analysis of deposits on CaF_2 windows. FTIR transmission spectra were recorded for thin deposits of oxidised samples of PEO, which were obtained by evaporation of aliquots of irradiated aqueous solution of PEO. The samples were dried at room temperature for 24 h. No buffer was used in order to avoid any contamination of the solution and any interaction with iron.

2.2. Chemical and spectrophotometric analysis

Chemical treatments of SF_4 and NH_3 were performed following the experimental procedure described previously [1].

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].

The pH was measured with an ORION pH-meter to ±0.1 pH unit.

Ion chromatographic analyses were performed. Aqueous solutions were injected directly without filtration. Working conditions are similar with those described in detail by Jaffrezo et al. [14]. DX 320 chromatograph (DIONEX) is equipped with an AS11 (4 mm) column for the anions in order to detect $HCOO^-$.

Infrared spectra were recorded with a Nicolet FTIR 760 spectrometer, working with OMNIC software. Spectra were obtained using 32 scans summation and $4\,cm^{-1}$ resolution. The calibration of the thickness (in μm) of samples was performed at $1965\,cm^{-1}$, which corresponds to a band combining (COC) stretching modes and (CH_2) rocking modes. The thickness (e) dependence on the absorbance at $1965\,cm^{-1}$ (OD) obeyed the equation: $OD = 0.00405 \times e$ [1]. UV-absorption spectra were recorded on a Varian spectrophotometer Cary 3.

The changes of molar weight (Mw, Mn), molar weight distribution (polydispersity index PI = Mw/Mn) and the intrinsic viscosity (IV) were obtained by size exclusion chromatography (SEC) analyses. Double distilled de-ionized water was used as eluent at a flow rate of $1\,mL\,min^{-1}$. A column was used for physical separation (TSK/Ref: GMPWXL). The refractive index was monitored continuously with a differential refractometer (Viscotek VE 3580) and the intrinsic viscosity with viscometer (Viscotek TriSec Model 270).

Total organic carbon (TOC) measurements in aqueous solution were obtained with a total organic carbon (TOC) analyzer Shimadzu model TOC-5050A. The Shimadzu TOC-5050A is

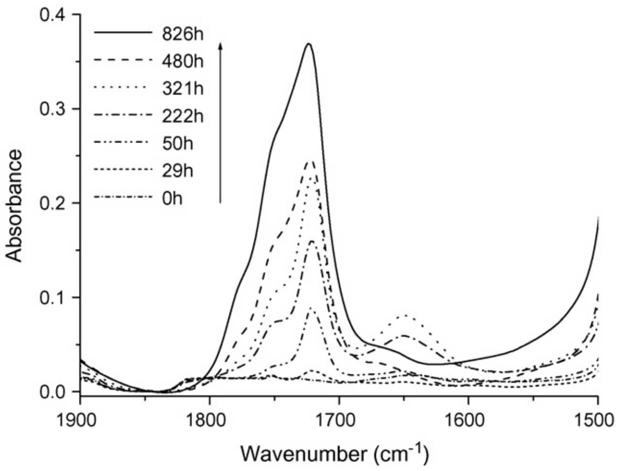


Fig. 1. FTIR spectra of deposits obtained from a PEO aqueous solution in the carbonyl domain (1900–1500 cm^{-1}) in the presence of Fe(III) during photooxidation (pH 3.1, [PEO] = 50.0 g L^{-1}, [Fe(III)] = 6 × 10^{-4} mol L^{-1}).

capable of performing total carbon (TC) analyses by combustion and inorganic carbon (IC) analyses by oxidation. 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 hydrogen carbonate with potassium carbonate for inorganic carbon.

3. Results and discussion

The oxidation of PEO photoinduced by Fe(III) (6 × 10^{-4} mol L^{-1}) ($\lambda \geq 300$ nm) in aqueous solution in the presence of oxygen at 15 °C was investigated at two different pH conditions: 3.1 and 7.8. First of all it is important to notice that no interaction between iron and PEO was observed in the medium.

3.1. pH 3.1

3.1.1. Analysis by IR spectroscopy

The FTIR spectra are limited to the domain of 4000–1000 cm^{-1} due to the opacity of the CaF_2 plate between 1000 and 400 cm^{-1}. Irradiation under wavelengths ($\lambda \geq 300$ nm, 15 °C) of PEO aqueous solution at pH 3.1 in the presence of Fe(III) leads to significant modifications of the IR spectrum (Fig. 1) characterised by the appearance of an absorption band at 1720 cm^{-1} (formate) and a shoulder around 1750 cm^{-1} (ester) in the carbonyl vibration region (1900–1500 cm^{-1}).

For irradiation times below 480 h, one can observe a preponderance of formates. After 480 h, a shoulder appears near 1770 cm^{-1}. This absorption band could indicate the formation of a secondary product resulting from hydrolysis or rearrangements of the photoproducts when pH is lower than 3.1. Indeed, the pH of the solution was observed to decrease after 480 h of irradiation from 3.1 to 2.5, as a result of the partial hydrolysis of formates in acid medium. Moreover, in the domain (1600–1200) cm^{-1}, the absorption bands of PEO are no more recognizable after 480 h of irradiation, which indicates that the structure of the polymeric backbone is drastically modified.

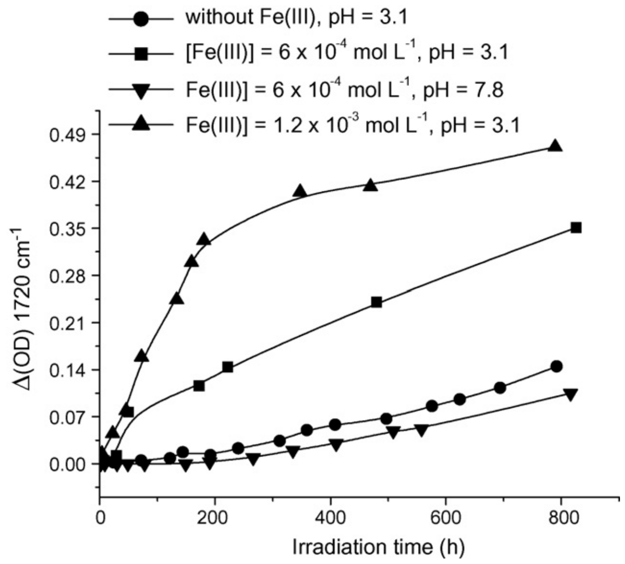


Fig. 2. Evolution of the absorbance at 1720 cm^{-1} as function of irradiation time in the absence or in the presence of Fe(III) at 6 × 10^{-4} and 1.2 × 10^{-3} mol L^{-1}, [PEO] = 50.0 g L^{-1}.

Comparison with the results previously obtained in the case of PEO aqueous solution irradiated in the absence of Fe(III) at pH 3.1 [3] shows that the same photoproducts are formed. If one considers the same absorption coefficients for the two C=O bands at 1750 and 1720 cm^{-1}, one can deduce from the previous results that the photooxidation of PEO in aqueous solution in the presence of Fe(III) results in the formation of four formate (end groups) to one ester (in the macromolecular chain) (ratio: 4/1). The same ratio is observed in the absence of Fe(III). These observations allow us to conclude that the mechanism of photooxidation of PEO in the absence as well as in the presence of Fe(III) is the same.

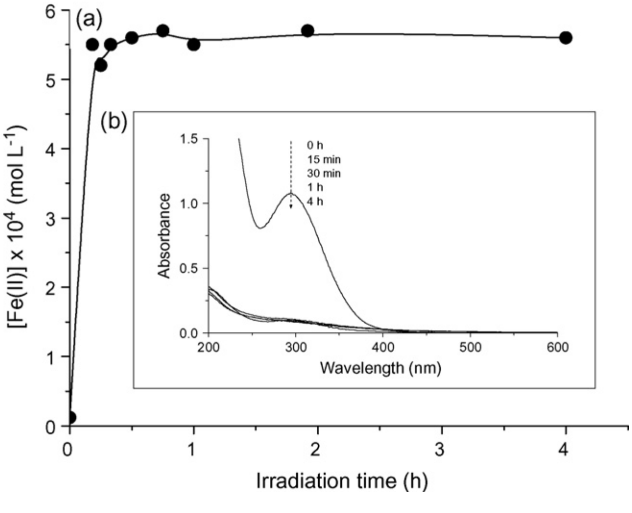


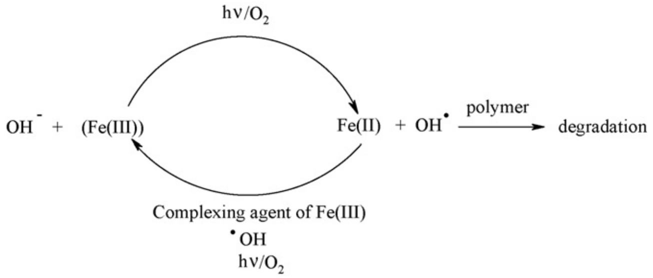
Fig. 3. (a) Fe(II) formation upon irradiation of PEO aqueous solution in presence of Fe(III) (initial pH 3.1, [PEO] = 0.1 g L^{-1}, [Fe(III)] = 6 × 10^{-4} mol L^{-1}) during photooxidation and (b) UV–vis spectra of PEO aqueous solution in presence of Fe(III) (initial pH 3.1, [PEO] = 0.1 g L^{-1}, [Fe(III)] = 6 × 10^{-4} mol L^{-1}) during photooxidation.

3.1.2. Kinetic of photooxidation of PEO

The variations of absorbance at 1720 cm^{-1} in presence and in absence of Fe(III) as a function of irradiation time in the case of the PEO aqueous solution at pH 3.1 are presented in Fig. 2 (this figure shows also the results concerning other pH and concentrations of iron, presented below in the manuscript). In order to compare different experiments, it was necessary to calibrate the thickness (*e*, in μm) of each deposit of the photooxidised sample. First of all, the curves show in Fig. 2 clearly that the rate of formation of carbonyl groups is much higher when the concentration of Fe(III) increases. In presence of Fe(III), two different slopes are observed on the kinetic curves of carbonyl groups formation.

Fig. 3 shows a very fast increase of 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). This photoreduction mainly leads to the production of $^{\bullet}OH$ radicals. After the first period of irradiation, Fe(II) concentration is constant and reaches an apparent-constant value corresponding to a photostationary equilibrium between Fe(III) and Fe(II) ([Fe(II)] ≈5.7×10^{-4} mol L^{-1} at the plateau) [15]. This photocatalytic process based on the couple Fe(III)/Fe(II) is presented in Scheme 1.

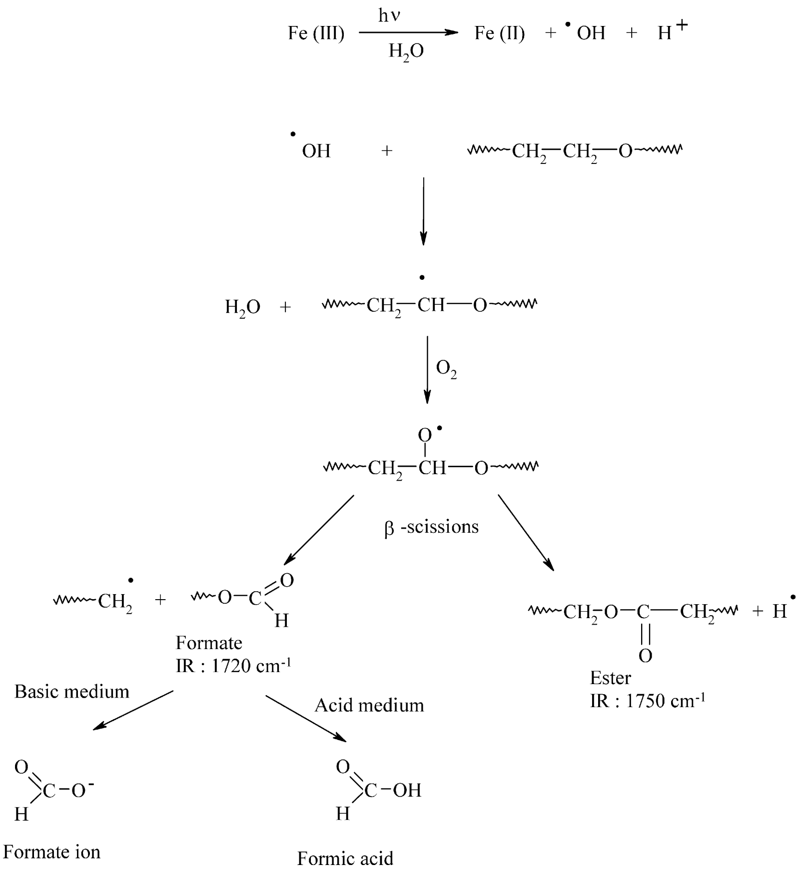
The first part of the photooxidation process, which is very fast, is then explained by the presence at $t = 0$ h of $Fe(OH)^{2+}$ which is an important photochemical source of $^{\bullet}OH$ radicals production (reaction 1). The concentration of Fe(II) was measured all along the irradiation (Fig. 3).



Scheme 1. Photostationary equilibrium between Fe(III) and Fe(II) in the presence of organic compounds, (Fe(III)) represents all species of ferric iron during the cycle Fe(III)/Fe(II)).

The second phase of the kinetic curves of the photooxidation of PEO aqueous solution in presence of Fe(III) (Fig. 2) corresponds to a decrease in the rate of formation of formate groups. This could 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 regularly formed in less important amount and also of the inherent photooxidation of PEO in aqueous solution.

The $^{\bullet}OH$ radicals react on PEO by hydrogen abstraction during the first step of oxidation mechanism. After reaction with oxygen alkoxy radical can lead to the formation of macromolecular formate and ester by β-scissions [16]. The partial hydrolysis of formate groups can occur, leading to formate ions. The following scheme summarizes the PEO photooxidation mechanism in the presence of iron:



3.1.3. Characterisation by SEC

The evolutions of the molar weight distribution during photooxidation are reported in Fig. 4. The changes caused by irradiation of the PEO aqueous solution in presence of Fe(III) are characterised by a shift of the molar weight distribution curves towards the lower molar weights. The number average molar weight decreased by about 70% after 50 h of irradiation and 94% after 170 h (Fig. 4). In PEO aqueous solution without Fe(III), Mw decreased about 10% after 50 h and 95% after 312 h. This decrease in the number average molar weight indicates that chain scissions occur.

The results show that chain scissions in PEO are dramatically accelerated by the presence of Fe(III) during the first hours of irradiation. As a consequence, this suggests that $^\bullet$OH radicals are involved in the photooxidation process.

These results can be correlated to the kinetics of photooxidation of PEO in aqueous solution shown in Fig. 2. They show the photoinductive effect of Fe(III) in water by formation of $^\bullet$OH radicals, which accelerates the photooxidation of the polymer and as a consequence, scissions of the macromolecular backbone.

3.1.4. Influence of the Fe(III) concentration

As recalled above the rate of photooxidation of PEO aqueous solution is strongly dependent on Fe(III) concentration. Fig. 2 shows that the formation of carbonyl products, and as a consequence the chain scissions, became faster when the concentration of Fe(III) increases. This effect can be correlated with the increase of the monomeric species present in Fe(III) solution. Indeed, the $Fe(OH)^{2+}$ species are the major light-absorbing species at 300 nm and the amount of $^\bullet$OH radicals produced is much higher for the Fe(III) concentration equal to 1.2×10^{-3} mol L^{-1}.

3.1.5. Influence of polymer concentration

The influence of the polymer concentration on the mechanism of degradation has been studied in the aqueous solution at pH 3.1, by comparison of PEO aqueous solutions at 50.0 and 5.0 g L^{-1}. The evolution of the pH during the irradiation has been also measured.

(a) Analysis by infrared spectroscopy

Solutions of PEO of two different concentrations (5.0 and 50.0 g L^{-1}) in presence of Fe(III) (6×10^{-4} mol L^{-1}) at pH 3.1 were irradiated. The comparison of the infrared spectra shows that the same photoproducts are formed in both cases. This indicates that the mechanism of photooxidation of PEO is not depending on the concentration of PEO in the solution.

(b) Characterisation by SEC

For both concentrations, the average number molar weight decreases as a function of irradiation time (Fig. 4). This can be attributed to chain scissions occurring in PEO macromolecular chains. The degradation of the polymer is accelerated in dilute aqueous solutions. Indeed, after 20 h of irradiation of the PEO aqueous solution at 5.0 g L^{-1}, the peak was shifted to longer retention time, which can be attributed to the formation of products with lower molar weight. However, this measure was out of range of the column separation. The degradation of PEO could be higher in diluted solution than in more concentrated solution because the mobility of polymer chains is higher in less viscous solution [2]. Moreover, this difference could be also explained by the fact that for a concentration of 50 g L^{-1}, PEO aqueous solution presents a notable diffusion of light. This diffusion effect could contribute to the decrease of the PEO phototransformation rate.

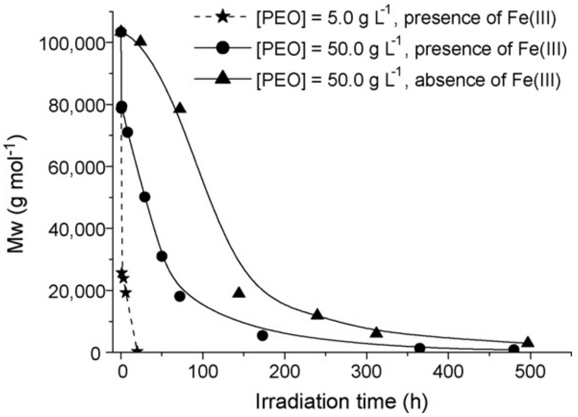


Fig. 4. Evolution of PEO molar weight (Mw) as a function of irradiation time in presence and in absence of iron ([Fe(III)] = 6×10^{-4} mol L^{-1}, pH 3.1, [PEO] = 5.0 and 50.0 g L^{-1}).

3.2. pH 7.8

Aqueous solutions of PEO were irradiated without acidification of the medium in the presence of Fe(III) in order to study the influence of the initial pH of the medium on the photodegradation of PEO in presence of iron. The initial pH of the PEO aqueous solution (50.0 g L^{-1}) changed from 8.4 to 7.8 after the addition of $Fe(ClO_4)_3$ (6×10^{-4} mol L^{-1}).

3.2.1. Analysis by infrared spectroscopy

UV-light irradiation of aerated PEO in aqueous solution (concentration 50.0 g L^{-1}, $pH_{initial}$ 8.4) in absence of Fe(III) leads also to the formation of formate end groups and esters and also to formate ions [3]. At a pH of 7.8, the same absorption bands are formed in the carbonyl region with the same stoechiometry.

3.2.2. Evolution of pH

The pH value decreased from 7.8 to 4.4 after 840 h of irradiation. In absence of Fe(III) at pH 8.4, the same dramatic decrease of the pH in the solution has been noticed [2]. This decrease has been correlated with the accumulation of formate ions ($HCOO^-$).

3.2.3. Effect of the presence of Fe(III)

Fig. 5 shows the variations of the absorbance at 1720 cm^{-1} and at 1750 cm^{-1} both in presence and in absence of Fe(III) as a function of irradiation time. It is observed that degradation of PEO appears more rapidly in presence of Fe(III). The degrada-

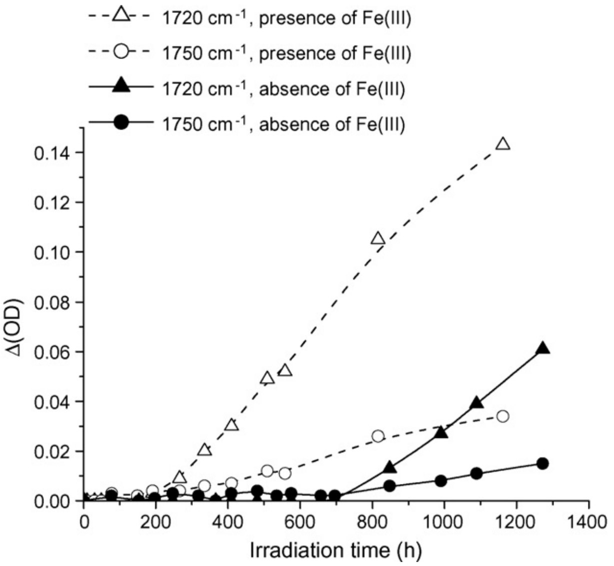


Fig. 5. Evolution of the absorbance at 1720 and 1750 cm^{-1} as function of irradiation time in presence and in absence of Fe(III) at pH 7.8 and 8.4, respectively ([PEO] = 50.0 g L^{-1}, [Fe(III)] = 6×10^{-4} mol L^{-1}).

tion of PEO in presence of Fe(III) can be observed after 200 h when the pH of the solution becomes lower than 7.0. This can be explained by the dissolution of Fe(III) when the pH of the solution decreases which increases the concentration of iron in water.

3.3. Influence of the pH in presence of Fe(III)

The rate of PEO photooxidation in aqueous solution in presence of Fe(III) is faster at pH 3.1 than at pH 7.8 at the beginning of irradiation (Fig. 2). Indeed, the rate of PEO photooxidation is strongly affected by the pH of the solution which controls the solubility and the speciation of Fe(III) monomeric species present in the solution. At pH 7.8, iron is not solubilised in aqueous solution. But the Fe(III) starts to be soluble in a weakly acidic medium (pH lower than 6.0) [9].

The nature and the concentration of Fe(III) species in the solution give evidences for the importance of iron speciation and consequently for photooxidoreduction process leading to Fe(II) formation and to oxidation of the PEO polymer present in aqueous solution [17].

3.4. Mineralisation of PEO

One of the aims of the present work was to test the efficiency of PEO removal from water solution, when the degradation was photoinduced by Fe(III). Total organic carbon experiments were undertaken in order to make evidence for the mineralisation of PEO. Relatively diluted polymer solutions (0.5 and 0.1 g L^{-1}) were chosen in order to point out the mineralisation of the polymer. As shown in Fig. 6a, total mineralisation of PEO was reached after 70 h of irradiation when the concentration of the solution was of 0.1 g L^{-1} and the pH 3.1. At higher concentration of PEO (0.5 g L^{-1}) (Fig. 6b), the mineralisation is slower and total after 320 h of irradiation. The complete mineralisation is obtained due to the continuous formation of radical species ($^{\bullet}$OH), which is the result of a photocatalytic cycle (Scheme 1), in homogeneous phase, based on the couple Fe(III)/Fe(II) and assisted by oxygen [15]. In the absence of Fe(III), no decrease of TOC concentration mineralisation was observed after 340 h of irradiation.

The rate of mineralisation under irradiation of PEO in aqueous solution in presence of iron was also examined. The results show the same rate of carbon disappearance (0.9 mg L^{-1} h^{-1}) for both concentrations of polymer solutions (0.1 and 0.5 g L^{-1}). This can be explained by the fact that the rate of degradation of PEO depends only on the initial concentration of Fe(III) species presents in the solution, in particular $Fe(OH)^{2+}$ species.

3.5. Thermooxidation

Thermooxidation at 50 °C of PEO aqueous solution in different pH conditions in presence of iron was studied in order to evaluate an eventual thermal effect on the degradation of

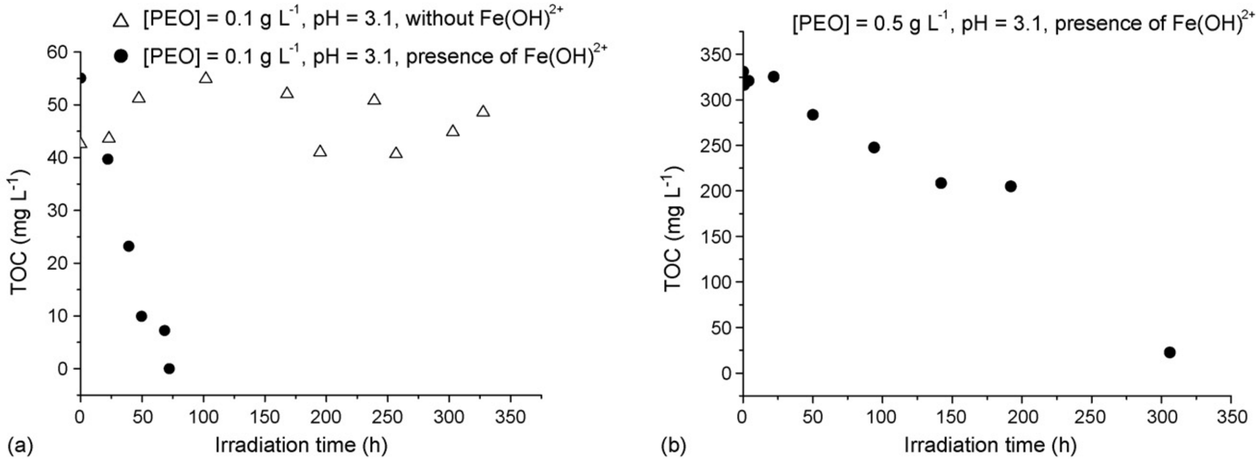


Fig. 6. TOC evolution of PEO aqueous solution during irradiation (λ ≥ 300 nm) (pH 3.1, [(Fe(III)] = 6×10^{-4} mol L^{-1}), (a) [PEO] = 0.1 g L^{-1} and (b) [PEO] = 0.5 g L^{-1}.

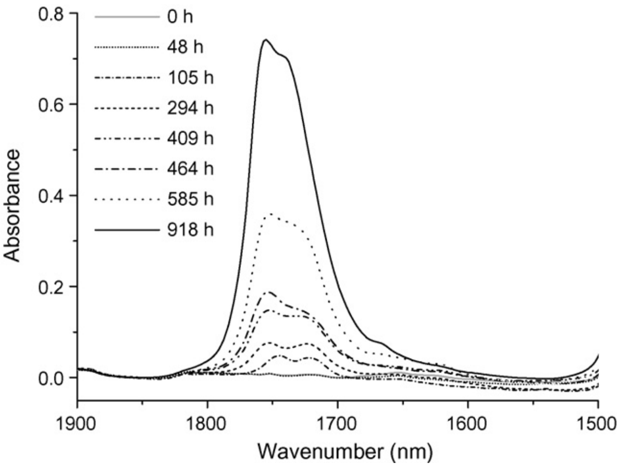


Fig. 7. FTIR spectra of deposits obtained from a PEO aqueous solution in presence of Fe(III) during thermooxidation (50 °C) ([PEO] = 50.0 g L^{-1}, [Fe(III)] = 6×10^{-4} mol L^{-1}, pH 3.1).

PEO aqueous solution. It is important to note that no significant oxidation of PEO, in the presence or in the absence of Fe(III), was observed even after 900 h at room temperature (20–25 °C).

At pH 7.8, in the absence and the presence of Fe(III), no significant evolution has been observed after 400 h of heating (50 °C) by infrared analysis contrary to pH 3.1.

3.5.1. Analysis by infrared spectroscopy

At pH 3.1, in the carbonyl region, two bands with an absorption maximum at 1750 cm^{-1} (ester) and 1720 cm^{-1} (formate) developed with similar intensities. For very long duration (900 h) a shoulder around 1735 cm^{-1} can be observed whereas the maximum at 1720 cm^{-1} is no more visible. For advanced times of irradiation, secondary products are observed (1735 cm^{-1}).

The comparison between the photooxidation and the thermooxidation of PEO in aqueous solution shows that the photooxidation generates formates in a ratio 4/1 against chain esters whereas thermooxidation produces equal amounts of esters and formates as already observed without iron [2,3] and in solid state [1] (Fig. 7).

3.5.2. Rate of thermooxidation of PEO at pH 3.1

The evolutions of absorbance at 1720 cm^{-1} in presence and in absence of Fe(III) as a function of heating time in the case of the PEO aqueous solution at pH 3.1 are reported in Fig. 8. This figure shows that the rate of carbonyl groups formation is much higher in PEO aqueous solution with Fe(III). It is probable that in presence of Fe(III), the redox mechanism (reaction 2) between iron species and the polymer with production of macroradicals is favoured by the temperature [18]. These macroradicals participate in the photooxidation of the polymer.

$$\sim\mathrm{CH_2{-}CH_2{-}O}\sim + \mathrm{Fe(OH)^{2+}} \xrightarrow{\Delta} \sim\mathrm{CH_2{-}\dot{C}H{-}O}\sim + \mathrm{Fe^{2+}} + \mathrm{H_2O} \tag{2}$$

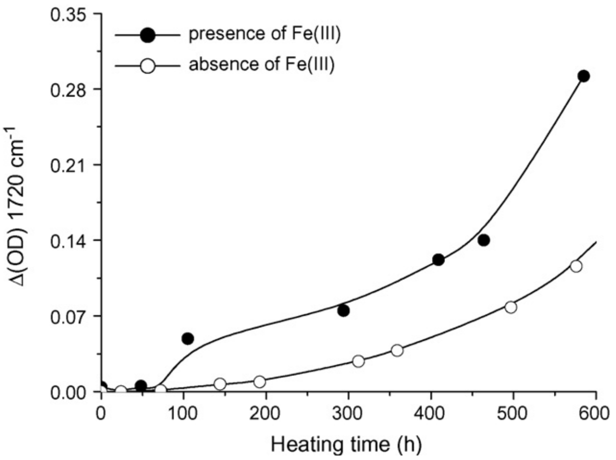


Fig. 8. Evolution of absorbance at 1720 cm^{-1} as a function of heating (50 °C) time in presence and in absence of Fe(III) ([PEO] = 50.0 g L^{-1}, [Fe(III)] = 6×10^{-4} mol L^{-1}, pH 3.1).

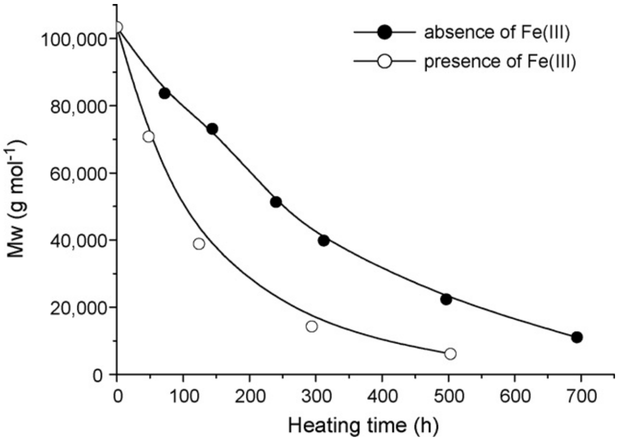


Fig. 9. Evolution of PEO molar weight (Mw) as a function of heating time ([PEO] = 50.0 g L^{-1}, [Fe(III)] = 6×10^{-4} mol L^{-1}, pH 3.1).

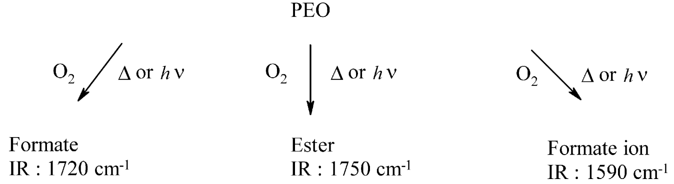
3.5.3. Characterisation by SEC

The evolutions of PEO during thermooxidation of aqueous solution at pH 3.1 in presence of Fe(III) was also characterised by SEC. Fig. 9 shows the decrease of the molar weight with no induction period both in presence and in absence of Fe(III). This decrease is attributed to chain scissions occurring in PEO chains, which indicate a dramatic degradation process during the thermal oxidation of the polymer. In presence of iron, the process of chain scissions is faster. This result shows again the efficiency of ferric salts in the acceleration of the degradation (oxidation) of PEO.

4. Conclusion

The results reported in this article show that the mechanism of photooxidation of PEO at different pH, concentration, in the presence or in the absence of Fe(III) is the same. Indeed, three photoproducts are observed: formate, ester and formate ions or formic acid. The formation of these last species depends on the pH of the medium. Formate ions or formic acid might come from partial hydrolysis of formate end groups of the polymer matrix, which explains the acidification of the medium. In conditions of thermooxidation, the same behaviour was observed. However, a difference in the ratio ester/formate was detected. In photooxidation, formate (end) groups were generated in a ratio 4/1 against (chain) esters, whereas in thermooxidation, equal amounts of esters and formates were produced.

These reactions can be summarised by the following scheme:



The presence of iron was observed to accelerate the rate of photooxidation or thermooxidation and as a consequence the degradation of the polymer. The addition of Fe(III), which increases the rate of PEO oxidation, is essential for the mineralisation of the polymer. Indeed, these results confirm that Fe(III) can act as an efficient photoinducer (at acidic pH) of PEO elimination from aqueous solution and that the photodegradation leads to the complete mineralisation. However, this study also demonstrates the importance of the Fe(III)/Fe(II) couple correlated with the pH of the medium during the photodegradation, and it is clear that at pH more relevant to aquatic environment (6–8) the effect of iron is very weak. Anyway, this work is the first one demonstrating that a water-soluble polymer can be completely mineralised in certain conditions (pH, iron and polymer concentrations).

References

[1] S. Morlat, J.L. Gardette, Polymer 42 (2001) 6071–6079.
[2] F. Hassouna, S. Morlat-Thérias, G. Mailhot, J.L. Gardette, Polym. Degrad. Stab. 92 (2007) 2042–2050.
[3] S. Morlat, J.L. Gardette, Polymer 44 (2003) 7891–7897.
[4] H. Kaczmarek, A. Kamińska, J. Kowalonek, A. Szalla, J. Photoch. Photobio. A 128 (1999) 121–127.
[5] H. Kaczmarek, J.F. Rabek, Angew. Makromol. Chem. 247 (1997) 11–130.
[6] H. Kaczmarek, A. Sionkowska, A. Kamińska, J. Kowalonek, M. Świątek, A. Szalla, Polym. Degrad. Stab. 73 (2001) 437–441.
[7] A.L. Lindén, J.F. Rabek, H. Kaczmarek, A. Kamińska, M. Scoponi, Coord. Chem. Rev. 125 (1993) 195–218.
[8] J.F. Rabek, A.L. Lindén, H. Kaczmarek, B.J. Qu, W.F. Shi, Polym. Degrad. Stab. 37 (1992) 33–40.
[9] C.M. Flynn Jr., Chem. Rev. 84 (1984) 31–41.
[10] R.N. Sylva, Rev. Pure. Appl. Chem. 22 (1972) 115–132.
[11] H.J. Benkelberg, P. Warneck, J. Phys. Chem. 99 (1995) 5214–5221.
[12] S.C. Philippart, J.L. Gardette, Polym. Degrad. Stab. 58 (1997) 261–268.
[13] J.G. Calvert, J.M. Pitts, Photochemistry, Wiley, New York, 1966, pp. 783–786.
[14] J.L. Jaffrezo, N. Calas, M. Bouchet, Atmos. Environ. 32 (1998) 2705–2708.
[15] L. Poulain, G. Mailhot, P. Wong-Wah-Chung, J. Photoch. Photobio. A 159 (2003) 81–88.
[16] C. Von-Sonntag, H.P. Schuchmann, Angew. Chem. Int. Ed. Engl. 30 (1991) 1229–1253.
[17] H. Mêšt'ánková, G. Mailhot, J.F. Pilichowski, J. Krýsa, J. Jirkovský, M. Bolte, Chemosphere 57 (2004) 1307–1315.
[18] P. Mazellier, M. Bolte, Chemosphere 35 (1997) 2181–2192.