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Phototransformation of water-soluble polymers. Part II: photooxidation of poly(ethylene oxide) in aqueous solution

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Abstract

Poly(ethylene oxide) (PEO) was irradiated in aqueous solution under long wavelengths ($\lambda > 300$ nm, 20 °C) and in presence of oxygen. The photooxidation of PEO was studied by IR spectrophotometry, viscometry and size exclusion chromatography. The formation of the oxidation photoproducts was studied by infrared analysis of films obtained by evaporation of aliquots of irradiated aqueous solutions. The photoproducts were identified by chemical derivatization treatments coupled with infrared measurements. Viscosimetry and SEC analysis showed that photooxidation was leading to a dramatic decrease of the molecular weights. The influence of the pH of the aqueous solutions was also examined. Unexpected results were obtained for the pH 12 solutions, indicating a strong inhibition of the oxidation.

Comparison with the results obtained in the case of PEO irradiated in the solid state showed that no direct transposition of the knowledge concerning the behavior of the solid polymer could be made.

Keywords: Poly(ethylene oxide); Photooxidation; Aqueous solution

1. Introduction

Poly(ethylene oxide) (PEO) is the simplest structure of water-soluble polymers. Water-soluble polymers are produced in large volumes and are widely used in a variety of industrial and consumer products. They find use in polymeric surfactant, pigment dispersants, mining oil drilling, detergents, etc. Some of these are also used in biomedical applications. After use, depending on their characteristics and particular applications, water-soluble polymers are discarded into solid waste disposal systems or as dilute aqueous solutions [1] and they are potential contributors to environmental problems.

This study of the photooxidation mechanism of PEO is part of a general study of water-soluble polymers carried out in our research group. Polyethers as solid polymers are very susceptible to oxidative degradation when exposed to UV irradiation in presence of oxygen, due to the formation of reactive intermediates such as free radicals and hydroperoxides. Modification of the chemical structure of polymers due to degradation leads to changes in the molecular weight, crystallinity and mechanical properties.

In this study, we investigated the photochemical behavior of two poly(ethylene oxide) samples (PEOlw and PEOhw) under irradiation at long wavelengths ($\lambda \geq 300$ nm, 35 °C) and in presence of oxygen, as these conditions of oxidation are these of the natural outdoor ageing. The thermooxidation at 50 °C is also studied because it permits a better understanding of the photooxidative behaviour.

The previous article [2] was dealing with the photooxidation of PEO in the solid state. The various photoproducts were identified and a general mechanism accounting for the photochemically induced oxidation of PEO was proposed. The objective of the present article is to investigate the behaviour of PEO irradiated in aqueous solutions and to compare it with the results of the solid state.

Numerous studies have addressed the challenge of understanding the complex degradation mechanisms of solid polymers, but to our best knowledge, the effect of UV radiation on aqueous solution of polymers has not been investigated so far.

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Transferring the data obtained for the solid state to aqueous solutions of the polymer is not obvious.

- The chemical nature of the chromophoric species should differ. In the case of 'non absorbing' solid polymer samples, it is generally admitted that the initiation of the chain oxidation results from the absorption of light by chromophoric defects or/and impurities resulting from the processing of the samples. One could question here about the importance of such chromophores.
- The influence of water on the structure and the reactivity of the reactive intermediates is likely to strongly modify the reactions in terms of kinetic and mechanism. The radical nature of the oxidation is highly questionable, radical mechanism is valid also in solution but ionic mechanism can also take place and very probably mixed mechanism should be considered.
- The mobility of the segments is totally different in aqueous solutions. Changes in macrochain order (conformation and crystallinity) have also to be considered as well as the mobility which is an important factor influencing the reactivity. In particular, the respective weight of propagation/termination by recombination of the radicalar species is likely to modify drastically the mechanisms.
- Reaction of water with some of the intermediate species or final products could occur. One has to pay attention to this point.
- The influence of the aquatic medium is likely to be totally modified with varying the pH of the solution. A generalisation of the results should take into account the influence of the pH.

For all these reasons, the analogy between the behaviour of PEO in the solid state and in aqueous solutions is really questionable and the fate of PEO in solution requires a strong effort to answer many questions that have been solved in the case of the solid state but that remain totally opened in the case of aqueous media.

Irradiated PEO aqueous solutions were characterised by IR spectrophotometry, viscometry and size exclusion chromatography (SEC). Depending on the polymer concentration and the pH value of the aqueous solution, the photooxidative behaviour of PEO was examined.

As recalled above, no extensive study has been reported on the photochemical degradation in aqueous solution. A few papers have been published, dealing with the behaviour of water-soluble polymers in organic solution, even with metal salts such as $FeCl_3$, $CuCl_2$, $CoCl_2$ or $NiCl_2$ [3–10]. This study concerning the simplest water-soluble polymer can be considered as a model to develop the experimental approach and the concepts adapted to a preliminary investigation of the mechanisms involved in the phototransformation of water-soluble polymers in aqueous medium.

2. Experimental

Poly(ethylene oxide) samples were supplied by Scientific Polymer Products. The approximate molecular weight of the two polymer samples was 100,000 and 4,000,000. In the present article, the samples are, respectively, denoted PEOlw and PEOhw.

Irradiations were carried out in a SEPAP 14/24 unit. The device is currently used to study the ageing of solid polymers, and peculiarly those polymers which necessitate irradiation at relatively low temperatures (e.g. < 40 °C). The chamber is an elliptical reactor equipped with one medium-pressure mercury lamp (Mazda MA 400) in vertical position at one axis of the chamber. Wavelengths below 300 nm are filtered by a glass enveloppe. The aqueous solution of PEO was irradiated in a Pyrex reactor cooled by water circulation. The temperature of the solution was maintained at 20 °C in order to avoid water evaporation. The reactor was placed at the second axis of the chamber.

Studies of PEO photodegradation were run in 1 or 10% water solutions, respectively, for PEOhw and PEOlw. Relatively concentrated polymer solutions were chosen in order to facilitate the determination of the chemical modifications of the irradiated solutions by IR analysis of deposits on CaF_2 windows. FTIR transmission spectra were recorded for thin films of photooxidised 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. Aqueous solutions of PEOlw were irradiated at three different pH values: $pH = 3$, 8 and 12. Solutions with $pH = 3$ and 12 were, respectively, obtained by adding drops of diluted HCl or NaOH. No buffer was used in order to avoid any contamination of the solution.

Infrared spectra were recorded with a Nicolet FTIR 760 spectrometer, working with OMNIC software. Spectra were obtained using 32 scan summations and 4 cm^{-1} resolution. A calibration of the thickness was described in part I [2] (e, in μm) of the non-photooxidised samples was performed by measuring the absorbance at 1965 cm^{-1}, which corresponds to a combination band of (COC) stretching modes and (CH_2) rocking modes [11,12]. Our results showed that the thickness dependence of the absorbance obeyed the equation: $OD = 0.00405 \times e$ for both PEO samples.

2.1. Chemical treatments

Chemical treatments with SF_4 and NH_3 were performed following the experimental procedure previously described [2,13–15].

Viscometry measurements were carried out in 1% water solutions at 30 ± 0.1 °C using an Ubbelöhde quartz viscometer.

The changes of molecular weight and molecular weight distribution (polydispersity index, M_w/M_n) were obtained by SEC using a WATERS chromatograph working with a Differential Refractometer detection and an Ultrahydrogel linear column in $NaNO_3$ 0.1 M. Ethylene glycol was added to the eluant phase to minimize hydrogen interactions. The equipment was calibrated with PEO standards.

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

3. Results and discussion

3.1. Analysis of the photooxidation by infrared spectroscopy

Infrared analysis were performed on deposits of aliquots of the polymer aqueous solution, which had a pH value of 8 before irradiation. The figures of FTIR spectra have to be limited to the domain 4000–1000 cm^{-1} due to the opacity of the CaF_2 plate between 1000 and 400 cm^{-1}.

The spectra of both poly(ethylene oxide) (PEOlw and PEOhw) before irradiation (obtained from a PEO aqueous solution deposit on CaF_2 plate) are exactly similar. Fig. 1 shows the spectrum of PEOlw.

Fig. 2 depict changes in the carbonyl region of spectra of samples obtained from aqueous solutions of both PEO samples ($pH = 8$) for several irradiation times ranging from 48 to 550 h. Fig. 2(a) shows the results obtained in the case of solutions of PEOlw (10% w/w). In the carbonyl region, three absorption bands develop. Two absorption bands appear and develop at 1750 and 1725 cm^{-1}. These bands can also be observed in the case of irradiation of solid samples [2]. A third band appears at 1585 cm^{-1} but the absorption maximum is progressively shifted towards 1595 cm^{-1} as irradiation proceeds. On the basis of chemical derivatization, the two first absorption bands have been attributed previously to the formation of formate (1725 cm^{-1} and also an absorption maximum at 1185 cm^{-1}) and ester (1750 cm^{-1}) groups [2].

Fig. 2(b) shows the IR spectra of solutions of PEOhw (1% w/w) irradiated for similar times. The modifications that are observed are similar to those described just above in the case of the lower molecular weight sample (PEOlw). The three same maxima are observed at 1750, 1725 and 1585 cm^{-1} that shifts to 1595 cm^{-1}.

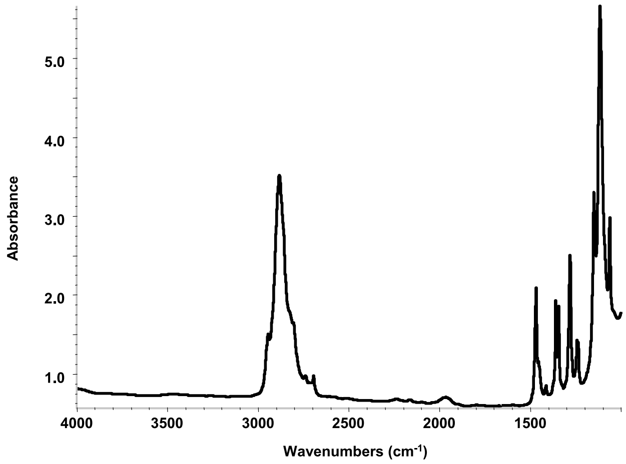

Fig. 1. FTIR spectrum of PEO before irradiation: deposit of PEOlw on CaF_2.

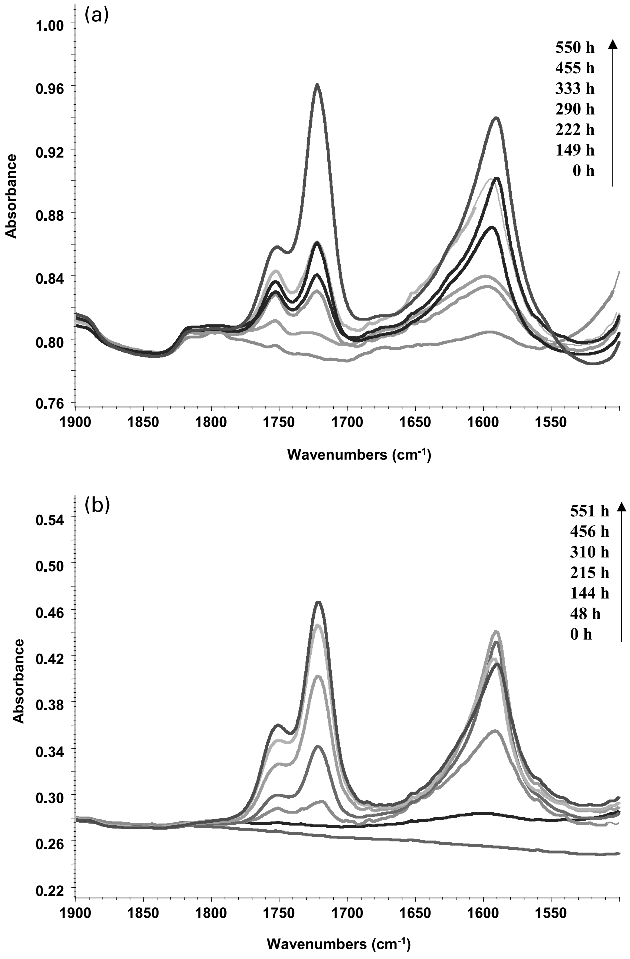

Fig. 2. FTIR spectra of PEO photooxidised in aqueous solution ($pH = 8$) at $\lambda > 300$ nm, 20 °C (in the range 1900–1500 cm^{-1}); (a) PEOlw (10% w/w), (b) PEOhw (1%).

The intense band that develop at 1595 cm^{-1} can probably be assigned to the C=O stretch of a carbonyl photoproduct. However, in order to identify precisely the product responsible for this absorption, complementary experiments were needed. Appropriate chemical treatments (SF_4, NH_3 and HCl) were performed on deposit of irradiated PEO.

3.1.1. SF_4

The reaction time with SF_4 had to be shortened and was reduced to 20 min, as longer time of treatment resulted in the destruction of the film. After SF_4 reaction, no absorption band between 1800 and 1850 cm^{-1} appeared on the IR spectra whereas the band at 1595 cm^{-1} collapsed (spectrum not shown). This behavior indicates clearly that the photoproduct corresponding to the absorption band at 1595 cm^{-1} reacts with SF_4, which should produce an acid fluorid, our result shows also that the acyl fluorid once formed by reaction with SF_4, are likely to migrate out of the polymer matrix and as a consequence are not detected by the analysis of the solid polymeric sample by infrared.

3.1.2. NH_3

The main changes that result from NH_3 treatment of a deposit of photooxidised PEOlw, are a decrease of the absorption band at 1725 cm^{-1}, and an increase of an absorption band at 1680 cm^{-1} (Fig. 3). These modifications indicate a reaction of NH_3 with formate at 1725 cm^{-1} groups to give formamide. It is worthy to note that, at opposite to the SF_4 treatment, no change are noticed concerning the absorption band at 1595 cm^{-1}.

3.1.3. HCl

HCl treatment was performed on a deposit of PEOlw which had been photooxidised for 350 h in aqueous solution. The IR spectra of photooxidised PEOlw were recorded before and after 5 min exposure to HCl vapours. The results are shown in Fig. 4. The treatment by HCl led to the total disappearance of the absorption band at 1595 cm^{-1} and also to the decrease of the absorbance at 1725 cm^{-1} corresponding to formate end groups. This derivatization by HCl gives evidence of a reaction between an acid and the photoproduct that absorbs at 1595 cm^{-1}.

3.1.4. Formic acid

In order to elucidate the chemical nature of this third photoproduct, a chemical treatment with formic acid was performed to introduce this molecular acid into a non irradiated PEO film [2]. The IR absorption bands of formic acid in the PEO matrix are centered at 1750 and 1725 cm^{-1}, respectively, for the monomer and the dimer form, but a third broad band centered at 1610 cm^{-1} can be noticed. In a second time, the PEO film was exposed to vapour of a neutralised solution of formic acid with NaOH. This treatment gave mainly an absorption band at 1610 cm^{-1}, which indicates unambiguously the presence of formic acid ions. On the basis of these results, the third photoproduct formed during photooxidation in aqueous solution can be attributed to formic acid ion.

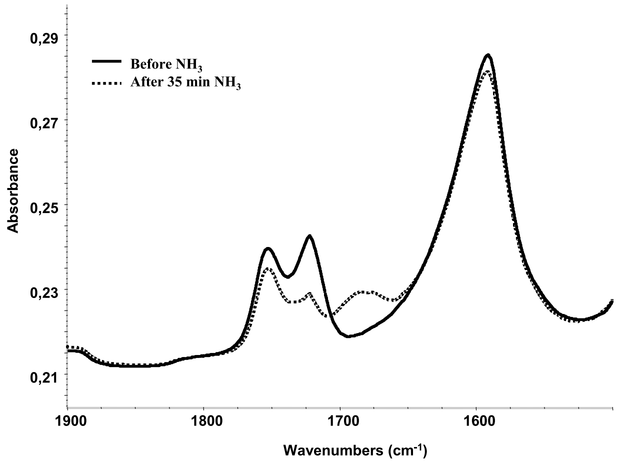

Fig. 3. NH_3 treatment of a PEOlw deposit after 290 h of photoxidation in aqueous solution (a) before treatment, (b) after 35 min exposure to ammonia treatment.

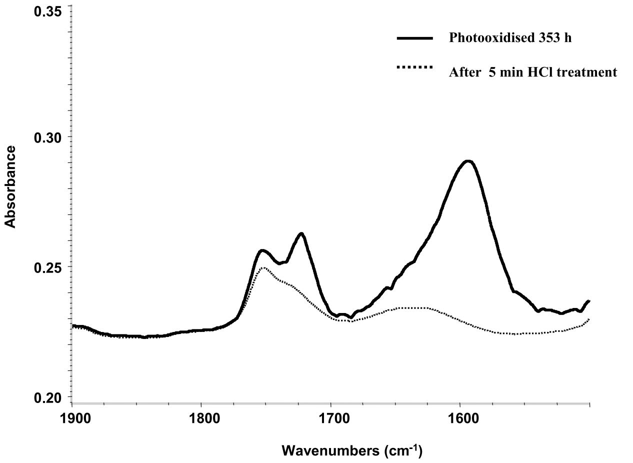

Fig. 4. HCl treatment of a PEOhw deposit (photoxidised 350 h in aqueous solution ($pH = 8$) at $\lambda > 300$ nm, 20 °C): (a) before HCl treatment, (b) after 5 min exposure to HCl vapours.

3.2. Photooxidation rate of aqueous solution of PEO

Fig. 5(a) shows the variations of absorbance at 1750, 1725 and 1595 cm^{-1} as a function of irradiation time in the case of an aqueous solution of PEOlw at $pH = 8$. It is recalled that in order to measure the variations of absorbance, it is at first necessary to calibrate the thickness (e, in μm) of each deposit of the photooxidised sample. The time dependence of these absorbances shows clearly that whereas the photoproducts identified, respectively, as ester (1750 cm^{-1}) and formate (1725 cm^{-1}) accumulate in the solution, the third photoproduct (1590 cm^{-1}) reaches a maximum concentration after around 200 h of irradiation and then decreases and stabilises after 300 h.

If one consider a same absorption coefficient for the two C=O stretches at 1750 and 1725 cm^{-1}, it can be deduced from our results that the photooxidation of PEOlw in aqueous solution at $pH = 8$ leads to the formation of three formate end groups to one ester function in the macromolecular chain. It is recalled that in the case of photooxidation in the solid state, this ratio was found higher (equal to 5) [2]. These data suggest that the third photoproduct corresponding to the absorption band at 1595 cm^{-1} might come from the partial hydrolysis of formate in water at pH 8.

As described above, the IR absorption band at 1595 cm^{-1} can be attributed to formic acid ions formed by hydrolysis of the formate groups because irradiations are carried out in an aquatic medium. After 500 h of irradiation, the pH of the solution was observed to dramatically decrease, from a value of 8 to 3. The acidification of the medium could be correlated to the release of formic acid functions in the aqueous solution.

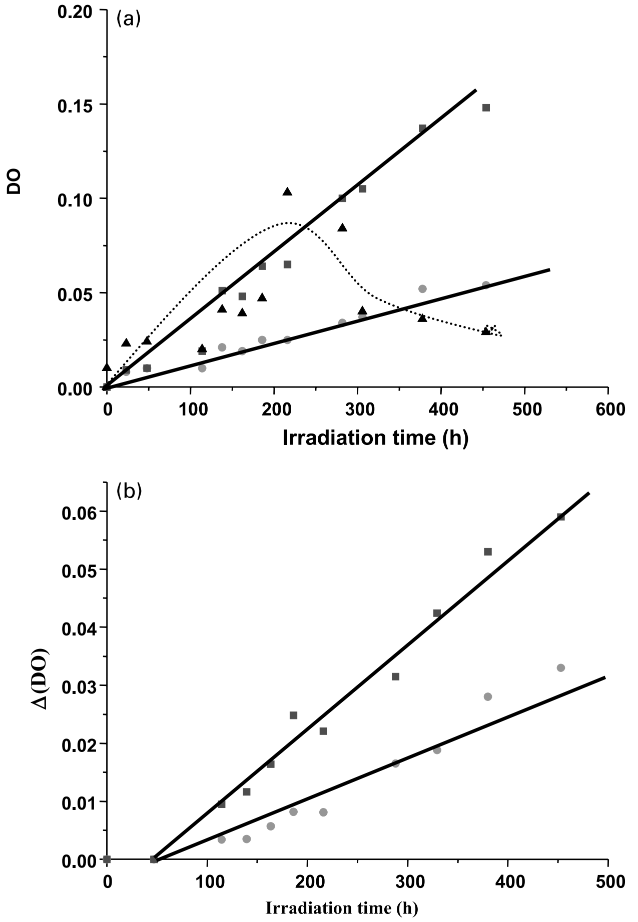

Fig. 5. Kinetic curves of formation of photoproducts during photooxidation of PEOlw in aqueous solutions (concentration of PEOlw 10%w/w); (a) pH = 8, (b) pH = 3.

3.3. Characterisation of irradiated PEO solutions

3.3.1. Viscometry

The intrinsic viscosity $[\eta]$ dropped from a value of 101 to 26 ml/g after 550 h of irradiation for a PEOlw aqueous solution. This decrease in viscosity can be attributed to main chain scissions occurring in PEO macromolecular chains, which indicates a dramatic degradation process taking place during the oxidation of the polymer.

3.3.2. SEC

For both polymers (PEOlw and PEOhw), the changes caused by irradiation of the polymer solution are characterised by a shift of the molecular weight distribution curves towards the lower molecular weights. An accurate determination was made in the case of PEOlw solution. In PEOlw aqueous solution (Fig. 6(a)), the number average molecular weight decreases by about 50% after only 150 h of irradiation and by 90% after 500 h. The narrowing of the chromatographic SEC curves for irradiated PEO indicates that the polymer becomes more uniform in terms of mass distribution. For PEOlw, the polydispersity decreases after irradiation (Table 1). In that case, main chain scissions are then predominant and the macromolecular weights approach similar values.

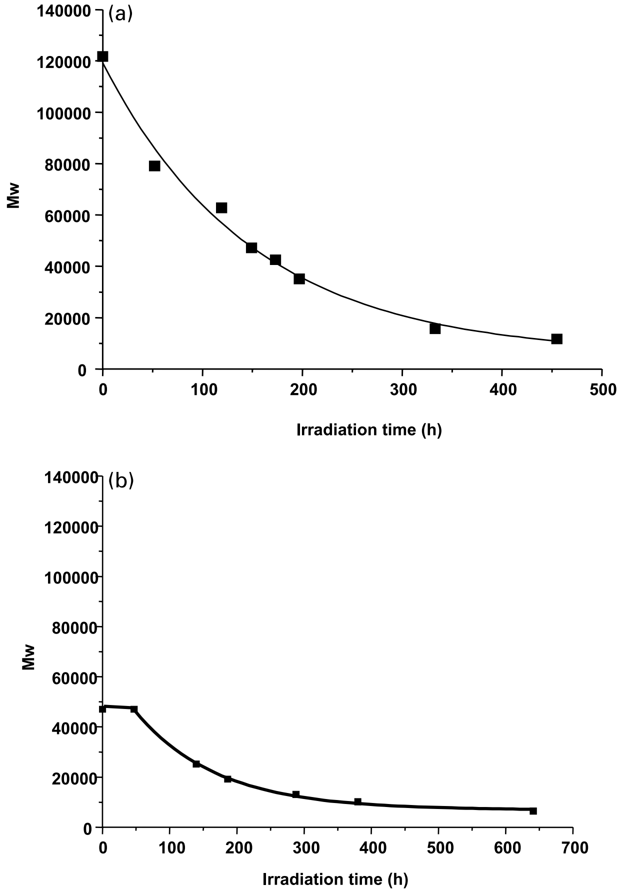

Fig. 6. Evolution of PEOlw molecular weight (M_w) in function of irradiation time for PEOlw aqueous solution; (a) pH = 8, (b) pH = 3.

Simultaneously, a new peak at longer retention time appears on chromatographic curves during irradiation (not shown here), which can be attributed to the formation of products with lower molecular weight. This is out of range of the column separation. Possible candidates could be oligomers or formic acid.

3.4. Influence of molecular weight

Irradiation of aqueous solution of PEOhw led to the same modifications of the molecular weight distribution curves as

Table 1
Evolution of the polydispersity index in function of irradiation time

Irradiation time (h)	Polydispersity index
0	6.1
52	5.9
119	4.9
149	4.8
197	4.3
290	4
455	3.7

observed in the case of PEOlw. An evolution towards lower molecular weight photoproducts was observed. The molecular weights of a PEOhw aqueous solution after 550 h of photooxidation were even lower than those of PEOlw.

3.5. Influence of the pH of the aquatic medium

Aqueous solutions of PEOlw were irradiated under different pH conditions: at pH = 3, 12 and 8. This last value can be obtained when the PEO polymer is dissolved in deionized ultrapure water.

3.5.1. Infrared characterisation

Fig. 7 compares the carbonyl regions of the IR spectra of PEOlw deposits after 550 h of irradiation of aqueous solution, with pH ranging from 3 to 12. This figure gives also the IR spectrum of a PEOhw solution at pH 8 after 550 h of irradiation.

These results are rather surprising. The spectra shown on Fig. 7 show indeed that at pH 3, only two photoproducts are detected (Fig. 7). These products have two absorption bands at 1725 and 1750 cm^{-1} (formates and esters). Moreover, their amount is much lower in an acidic medium than at pH 8. The relative proportion of each band is quite different as previously observed, as the absorbances of each band are nearly equivalent. Surprisingly at pH 12, no carbonyl band develops during the same irradiation time.

3.5.2. SEC analysis

The aqueous solutions of PEOlw (at pH 3 and pH 12) were also characterised by SEC during photooxidation.

3.5.3. Acidic medium pH = 3

Fig. 6(b) shows that the chromatographic SEC curve of PEOlw before irradiation in an acidic medium (pH 3) is shifted towards longer retention times. These data suggest that the macromolecular chains of PEO are modified in acidic medium. As irradiation proceeds, the molecular weight distribution curves are also shifted to lower molecular weights but one can notice that no modification occur during the first 50 h (Fig. 6(b)). Similar observations are deduced from the infrared analysis (not shown) that shows an induction period for 50 h where no carbonyl products is detected. These results confirm that chain scissions occur during photooxidation in acidic medium as already observed in solution at pH 8, which is in good accordance with the IR observations.

3.5.4. Basic medium pH = 12

It is recalled that the infrared analysis shows that no product is formed even after relatively long irradiation times (520 h). The chromatographic SEC curves (Fig. 8) confirm totally these observations and show that no evolution occur during irradiation until 520 h, which is reported above on the basis of the infrared analysis.

Our data show a dramatic influence of the pH on the photooxidation of PEO aqueous solutions. Important conclusions can be deduced from our experiments. PEO appears as rather photostable in basic medium whereas in a neutral aquatic compartment, the formation of three photoproducts is observed. The release of formic acid ions leads to an acidification of the medium. At pH 3, the formic acid ions are not detected as the equilibrium is shifted to the acidic form.

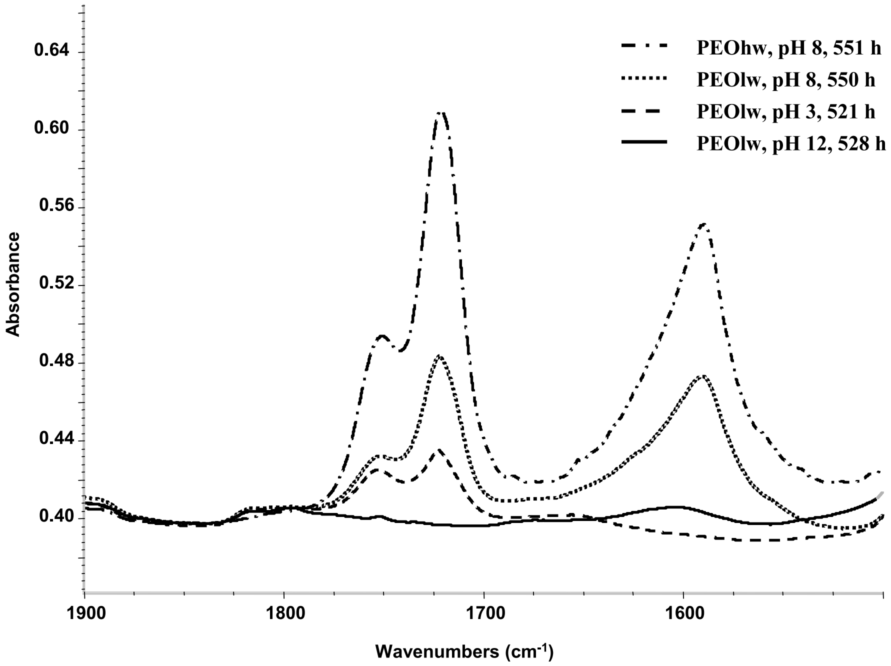

Fig. 7. FTIR spectra of PEO photooxidised 520 h in aqueous solution at λ > 300 nm, 20 °C: (a) PEOlw, pH = 8, (b) PEOhw, pH = 8, (c) PEOlw, pH = 3, (d) PEOlw, pH = 12.

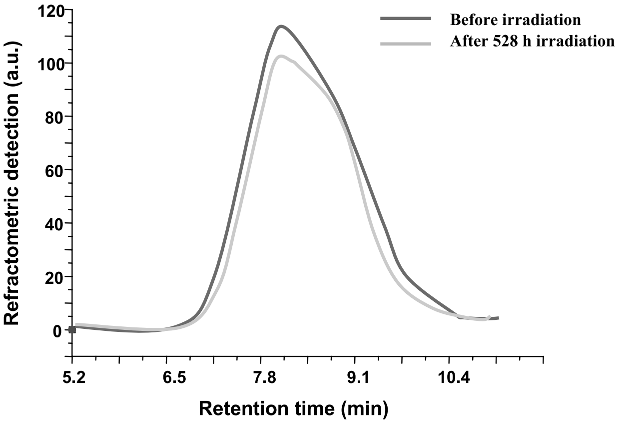

Fig. 8. SEC chromatograms of PEOlw aqueous solution at pH 12 during photooxidation.

This first study on phototransformation of a water-soluble polyether in aqueous solution shows that in no way, the results obtained in the solid state can be transposed to the aqueous medium. This is true in terms of mechanism. It has been shown formerly that the rate constant of reaction of HO• radicals with polymers depends on both the concentration and the molecular weight of the polymer [16] and also on the pH of solution. Moreover, the matrix effects are totally different. In crystalline solid state, PEO exists mainly in form of regular 7_2 helix [10], whereas the PEO chain in water behaves as a flexible polymer with a relatively large hydrodynamic diameter [17]. Unusual phenomena observed in water have been exclusively ascribed to the specificity of water as a solvent and the local conformation of the PEO chain is still subject to controversy.

4. Conclusion

A peculiar attention was given to the photooxidation carried out at long wavelengths ($\lambda > 300$ nm) as these conditions of irradiation are those of the natural outdoor ageing. The corresponding oxidation mechanism is of prime importance to account for the evolution of water soluble polymers in aquatic media.

It can be recalled briefly that, in solid medium, the photooxidation at long wavelengths ($\lambda > 300$ nm) occurs through a conventional radical mechanism involving the formation of secondary hydroperoxides on the carbon atoms in the α-position to the oxygen atom [2].

We must conclude that the degradation mechanisms for solid samples and aqueous solutions are significantly different. Our results permit comparing the photooxidation of PEO in the solid state and in aqueous solution. Both investigations were carried out under similar experimental conditions for the wavelengths of irradiation ($\lambda > 300$ nm) and the presence of oxygen. Only the temperature was different (35 °C for films in solid state and 20 °C in aqueous solution).

This study confirms that PEO is a very sensitive polymer towards photooxidation in the solid state and also in aqueous solutions. Photochemically induced oxidation is responsible for a rapid damage of the macromolecular chain as the major carbonylated products that are formed are formate end groups. Numerous chain scissions occur and in aquatic media, the release of formic acid ions is also observed.

The main difference between the photoproducts formed in conditions of photooxidation in the solid state and in aqueous solution concerns the formation of formic acid ions in neutral medium, which leads to the acidification of the aquatic compartment.

The photoproducts formed by irradiations of PEO in aqueous solution depend on the pH value of the medium. However, these preliminary results do not permit concluding that photooxidation proceeds by the same mechanisms in both conditions. A strong influence of the pH of the aqueous solution is observed on the photochemical behaviour of PEO, which cannot be explained if one consider only the chemical structure of the polymer.

Our experimental results could indicate the importance of ionic reactions in the photooxidation process occurring in aqueous media. However, one may question about the close reactivities observed in the solid state and in acidic or neutral aqueous media, since only radicalar reactions occur in the solid polymer. This point necessitates complementary studies that have been engaged and will be published in a forthcoming paper.

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