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Phototransformation of water-soluble polymers. I: photo- and thermooxidation of poly(ethylene oxide) in solid state

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Abstract

The photooxidation of two poly(ethylene oxide) samples (PEOlw $M = 10^5$ and PEOhw $M = 4 \times 10^6$) has been studied under irradiation at long wavelengths ($\lambda \geq 300$ nm, 35°C) and in the presence of oxygen. Thermooxidation experiments, at 50°C, of PEO samples are also reported and compared to photooxidation results. Differences in the ratio ester/formates are observed. Thermooxidation produces equal amounts of esters and formates whereas photooxidation generates formates in a ratio of 5/1 against chain esters. The oxidation kinetic curves were plotted for films of thickness less than 40 μm to avoid heterogeneous degradation. In order to identify the oxidation products, photo- and thermooxidised films have been submitted to chemical treatments. A mechanism accounting for the main routes of oxidation is proposed. The differences between thermooxidation and photooxidation are explained on the basis of different evolutions of the macroperoxyradicals $POO^{\cdot}$. The formation of hydroperoxides is favoured in thermooxidation whereas recombination of the peroxyradicals is more likely to occur in photooxidation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Water-soluble polymer; Poly(ethylene oxide); Photooxidation

1. Introduction

Poly(ethylene oxide) (PEO) is the simplest structure of water-soluble polymers and among the polyethers, PEO and PVME are the only ones readily soluble in water [1]. PEO is a biocompatible, biodegradable, non-ionic water-soluble polymer of considerable industrial significance. High-molecular-weight PEO can be used in packaging, particularly one-use packaging and agricultural films. After use, depending on their characteristics and particular applications, water-soluble polymers are discarded as dilute aqueous solutions or into solid waste disposal systems [2].

Water-soluble polymers are potential contributors to environmental problems. This study of the photooxidation mechanism of PEO in solid state is part of a general study of water-soluble polymers carried out in our research group. In the aim to better understand the evolution of the water-soluble polymers in the aquatic environment, it is necessary to determine previously the mechanism of degradation in the solid state. The results obtained in the case of irradiation of PEO in aqueous solution is currently under investigations and will be presented in a forthcoming paper.

The photo- and thermooxidation of PEO has not received specific attention. Most studies concerning polyethers have dealt with low molecular weight polyethers such as poly(ethylene glycol) (PEG) with molecular weight value below 25,000. Several studies carried out in our group have dealt with the photochemical behaviour of polyethers [3]. Most of the research work was devoted to copolymers such as copoly(ether-ester) thermoplastic elastomers [4], polyether-*block*-polyamides [5–7] aromatic and aliphatic poly(ether-urethane) [8], fluorinated polyethers [9] and blends of polystyrene/poly(vinylmethylether) (PS/PVME) [10], but only few homopolymers were studied: PEG [6,7], polypropylene glycol (PPG) [6,7], polytetramethylene glycol (PTMG) [5,7], PVME [11], poly(vinyl ethyl ether) and poly(vinyl isobutyl ether) [9,12].

Films of PEO with alkali metal salts (such as NaCNS, $LiClO_4$,...) have also been studied in terms of thermal or thermooxidative stability because of their potential as electrolytes in high-energy-density batteries [13–18].

The first step of our study of PEO was to elucidate the mechanism of photodegradation in the solid state in order to better understand afterward the phototransformations in aqueous solution. The present article reports on the photochemical behaviour of PEO of high molecular weight. PEO samples of two different molecular weights have been studied under irradiation at long wavelengths

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(at $\lambda \geq 300$ nm, 35°C) and in the presence of oxygen. The oxidation products are analysed by FTIR spectroscopy, coupled to chemical treatments in order to identify the photoproducts. On the basis of photooxidation results compared to those obtained for thermooxidation experiments, a degradation mechanism will be proposed.

2. Experimental

PEO samples were supplied by Scientific Polymer Products. The approximate molecular weight of the two polymer samples was 100 000 and 4 000 000, these samples were respectively denoted PEOlw and PEOhw.

Films, 20–40 μm thickness, were made by compression moulding between PTFE-coated glass cloth at 200 bar for 1 min at 100°C for PEOlw and 120°C for PEOhw. Thinner films (less than 20 μm thickness) were obtained by evaporation of aliquots of an aqueous solution of PEO on CaF_2 plates.

Irradiations 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 [19]. 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 envelope. At the second axis of the chamber, the samples were fixed on a rotating carousel of 13 cm diameter which can receive 24 samples. In this series of experiments, the temperature at the surface of the samples was fixed at 35°C in order to operate below the melting point of PEO (mp = 65°C).

'Low temperature' thermooxidation experiments were carried out in air ovens at 50°C to keep the films in solid state at a temperature below their melting point.

Infrared spectra were recorded with a Nicolet 760-FTIR spectrometer, working with OMNIC software. Spectra were obtained using 32 scan summations and a 4 cm^{-1} resolution. A calibration of the thickness (e, in μm) of the non-photooxidised samples was performed at 1965 cm^{-1}, which corresponds to a combination band of (COC) stretching modes and (CH_2) rocking modes [20,21]. The thickness dependence of the absorbance obeyed the equation: $OD = 0.00405 \times e$ for both PEO samples.

The photooxidised samples were submitted to various chemical treatments in order to identify the photoproducts. The irradiated films were exposed to reactive gas, at room temperature, in a simple flow system that could be sealed off to permit the reaction to proceed. In parallel to those treatments, it was verified that the non-oxidised polymers were not reacting with the gas. SF_4 and NH_3 treatments were carried out in an all Teflon systems. Acid groups react with SF_4 to give acid fluorides.

$$RCOOH \xrightarrow{SF_4} RCOF$$

The absorption band ν(C=O) of acid fluorides has a characteristic wavenumber between 1800 and 1850 cm^{-1} [5,22]. SF_4 reacts with all –OH groups and as a result, the absorption in the hydroxyl region decreases [23].

Acid groups also react with NH_3 to give ammonium carboxylates and esters by reacting with NH_3 produce amide groups.

$$RCOOH \xrightarrow{NH_3} RCOO^-,\ NH_4^+$$

$$RCOOR' + NH_3 \rightarrow RCONH_2 + R'OH$$

The ammonium carboxylates are characterised by an infrared absorption band above 1550 cm^{-1}. Amide groups present among others, two characteristic absorption bands around 1670 cm^{-1} (amide I band) and 1630 cm^{-1} (amide II band).

3. Results and discussion

Analysis of changes in the IR spectra requires that the absorption bands composing the spectrum of the PEO before irradiation (Fig. 1) are identified. The main spectral features of the PEO polymer are presented in Table 1.

3.1. Analysis of the photooxidation by infrared spectroscopy

Films of PEOlw and PEOhw were irradiated in the SEPAP 14-24 unit at $\lambda \geq 300$ nm and 35°C.

Irradiation of films of PEO leads to important evolutions of the IR spectrum characterised by the appearance of new absorption bands in the carbonyl vibration region (1900–1500 cm^{-1}) (Fig. 2a). In the carbonyl region, a band with an absorption maximum at 1725 cm^{-1} develops and a shoulder around 1750 cm^{-1} is observed. Fig. 2b shows that, in the domain between 1500 and 900 cm^{-1}, all the absorption bands tend to decrease whereas a shoulder arose at 1185 cm^{-1}. These maxima can be attributed to the formation of formate (1725 and 1185 cm^{-1}) and ester (1750 cm^{-1}) groups [8].

Quantitative results cannot be obtained by measuring the diminution of absorbance of the ν(C–O–C) band at

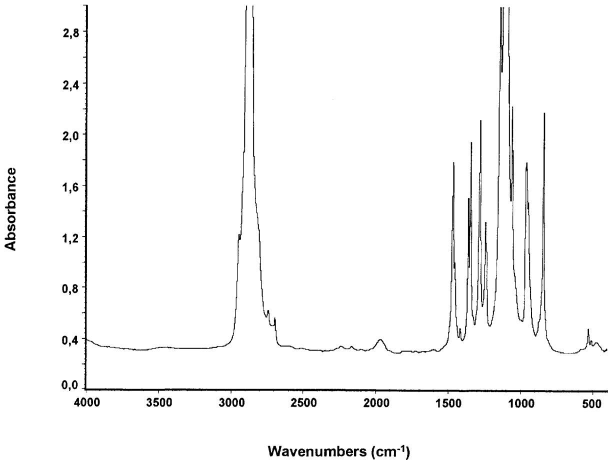


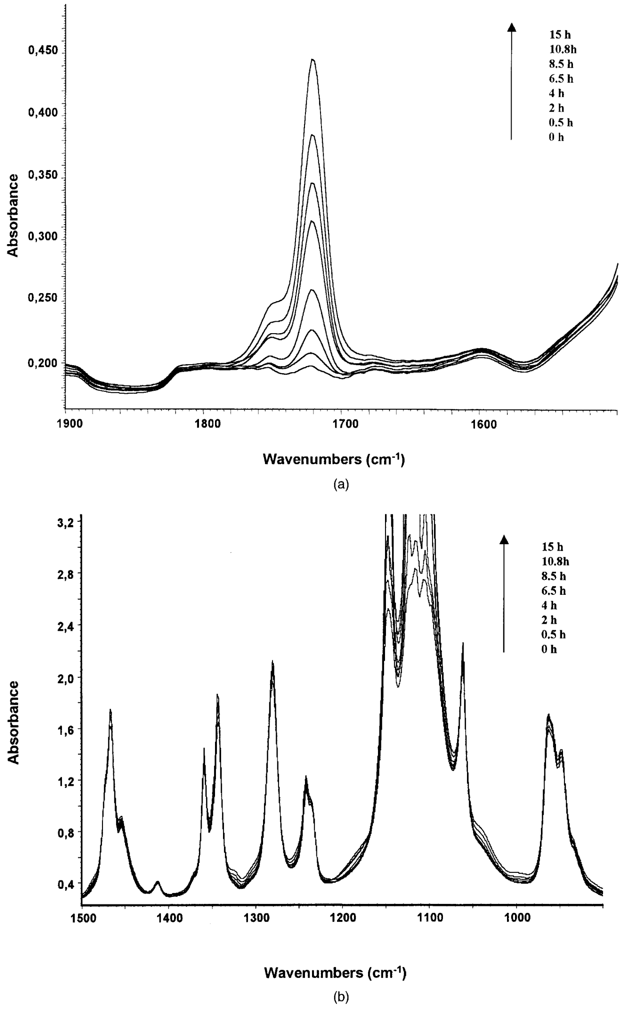
Fig. 1. FTIR spectrum of a PEOlw film before irradiation.

Table 1
Attribution of infrared absorption bands of poly(ethylene oxide) film (identification based on analysis of the literature data [20,21] and comparison with low molecular weight PEG)

ν (cm^{-1})	Attribution
2950	Antisym. stretching (CH_2)
2880	Sym. stretching (CH_2)
1965	(C–O–C) stretching + CH_2 rocking
1465 → 1413	Bending (CH_2)
1360, 1345	Bending (CH_2)
1280–1240	Bending (CH_2)
1150 → 1060	Antisym. stretching (C–O–C)

1115 cm^{-1} as far as this ether band is too intense even for thin films.

Irradiation had to be limited to moderate extents of oxidation because the samples were becoming too brittle, especially in the case of thin films.



(a)

(b)

Fig. 2. FTIR spectra of a PEOlw film photooxidised at $\lambda \geq 300$ nm, 35°C (film thickness 22 μm) (a) in the domain 1900–1500 cm^{-1} and (b) in the domain 1500–900 cm^{-1}.

3.2. Chemical treatments of photooxidised samples

Derivatisation reactions have been carried out to identify the oxidation photoproducts the formation of which is observed in the carbonyl region of the IR spectrum. These reactions are carried out by treating photooxidised samples with gaseous reactants (sulfur tetrafluoride, ammonia). The reaction time was reduced to 20 min with SF_4, longer time of exposure resulting in the film destruction, but NH_3 treatments were left 1 h to allow the reaction to proceed.

3.2.1. SF_4 treatment

The spectra before and after SF_4 reaction are similar and no absorption band between 1800 and 1850 cm^{-1} appears. SF_4 treatment does not give evidence of the presence of acid in photooxidised film of PEO.

3.2.2. NH_3 treatment

In the carbonyl vibration region (Fig. 3), one observes a decrease of the main oxidation band at 1725 cm^{-1} correlated with an increase of two bands at 1680 and 1595 cm^{-1}.

NH_3 reacts with esters to produce amides. In this case, NH_3 reacts with formate end groups to give formamide, the corresponding absorption band is observed at 1680 cm^{-1}. In basic medium, formate can also undergo a saponification reaction leading to the formation of the ammonium salt of formic acid. An absorption band at 1605 cm^{-1} has already been observed by reaction of a photooxidised PTMG film with NaOH [7], the saponification of formate giving rise to formate ions. The band at 1595 cm^{-1} can be attributed to the formation of ammonium carboxylates.

3.3. Kinetic study of the photooxidation of PEO

Depending on the conditions in which ageing is carried out, heterogeneous effects can be produced. The most widespread cause of heterogeneous degradation at the macroscopic level results from oxygen diffusion-limited effects [24]. These effects depend on several parameters, such as sample thickness, coupled with the oxygen consumption rate which depends on the reactivity of the polymer and the oxygen permeability of the material.

Infrared spectroscopy permits monitoring the effect of heterogeneous oxidation. The evolution of absorbance measured at 1725 cm^{-1} (corresponding to the maximum in the carbonyl vibration region) for PEOlw and PEOhw was plotted as a function of the thickness of the photooxidised films (after 6 h) (Fig. 4).

The absorbance varies linearly with the thickness up to 40 μm, which indicates that oxidation occurs homogeneously in the film. Above 40 μm thickness, a deviation from the linearity is observed, suggesting that oxygen starvation occurred. This effect can be avoided by reducing the thickness of the samples below 40 μm, which ensures that no limitation of the oxidation rate by oxygen diffusion occurs.

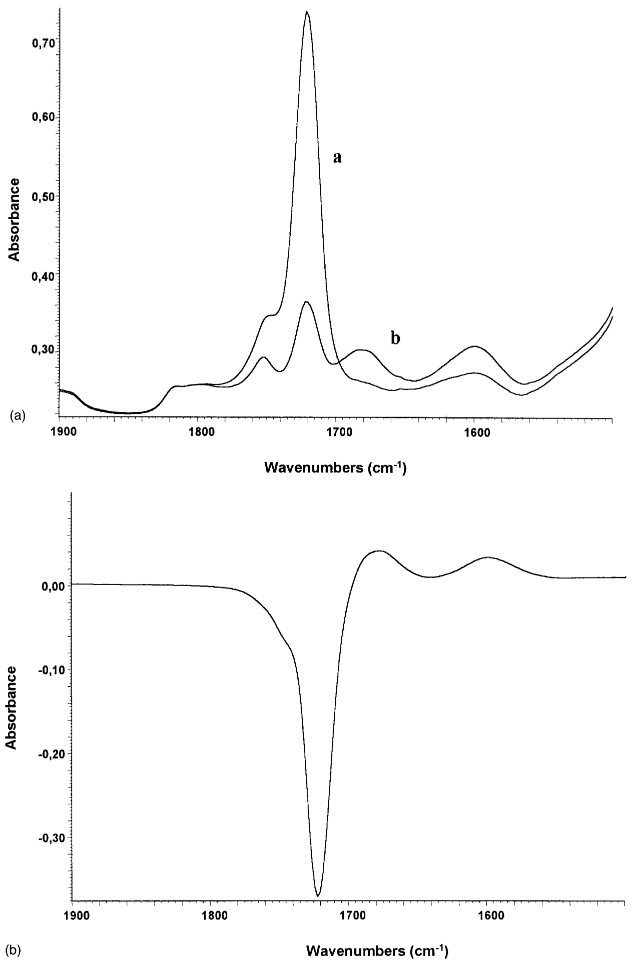


Fig. 3. NH_3 treatment of a PEOlw film photooxidised for 15 h at $\lambda \geq 300$ nm, 35°C, thickness 110 μm. Direct spectra (top) and subtracted spectrum between the irradiated and the treated film (bottom).

3.4. Photooxidation rate

The photooxidation rates were directly compared in the case of films with a thickness below 40 μm.

Fig. 5 shows the variations of absorbance at 1725 cm^{-1} for PEOlw and PEOhw films (thickness ≤40 μm) as a function of irradiation time. The results indicate that the rate of carbonyl groups formation is slightly higher for PEOlw than for PEOhw.

This weak difference between PEOlw and PEOhw could not be explained by an effect of PEO crystallinity. It is known that in semi-crystalline polymer like PEO, photooxidative degradation starts in the amorphous phase because of easier diffusion of oxygen to the unordered macrochains than to the rigid crystalline regions where the access of oxygen is restricted [25]. The crystallinity of both PEO were determined by differential scanning calorimetry (DSC), taking for the enthalpy of melting of a 100% pure crystalline PEO, the value $\Delta H°m = 220.81$ J/G [25]. DSC analysis shows that in PEOlw, the crystalline phase represents 83% of the sample whereas PEOhw contains only 60% of crystalline PEO [25].

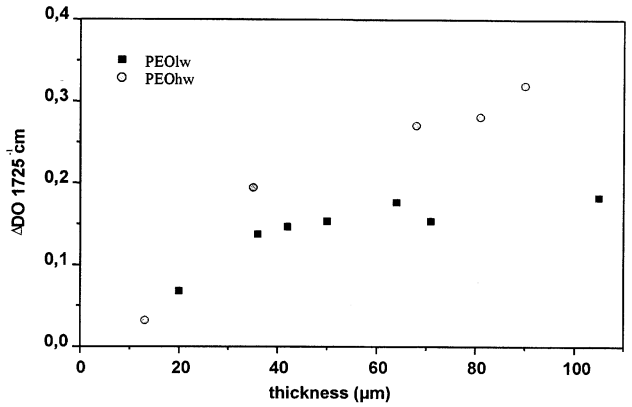


Fig. 4. Evolution of absorbance at 1725 cm^{-1} as a function of film thickness for PEO films photooxidised for 6 h. (a) PEOlw. (b) PEOhw.

3.5. Thermooxidation

The behaviour of the PEOlw and PEOhw polymers is quite different throughout thermooxidation, even if the temperature is not as high as usual in the degradation experiment of polymers, it is recalled that thermooxidation of PEOlw and PEOhw was carried out at 50°C.

3.5.1. Changes in the IR spectra

In the carbonyl region, important changes are observed in the IR spectra (Fig. 6).

Whereas PEOlw still develops two absorption bands with maxima at 1750 and 1725 cm^{-1}, in the case of PEOhw, one observes a third absorption band at 1610 cm^{-1}. Moreover, the relative proportion of ester is much higher in the case of thermooxidation than in the case of photooxidation. Thermooxidation of a film of PEOlw (or PEOhw) leads to the formation of ester and formate in the same extent whereas photooxidised films develop five formate end groups to one ester function in the macromolecular chain (considering a same absorption coefficient at 1750 and 1725 cm^{-1}). A

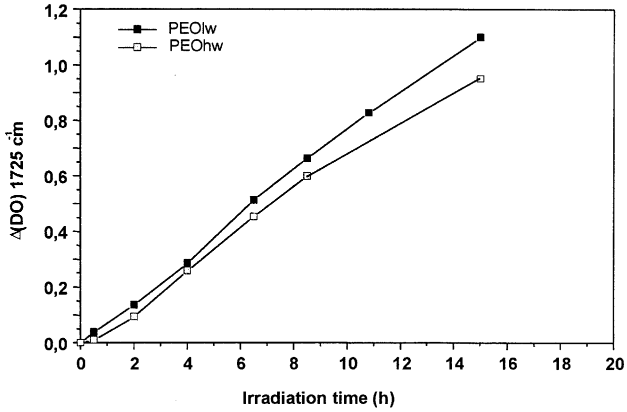
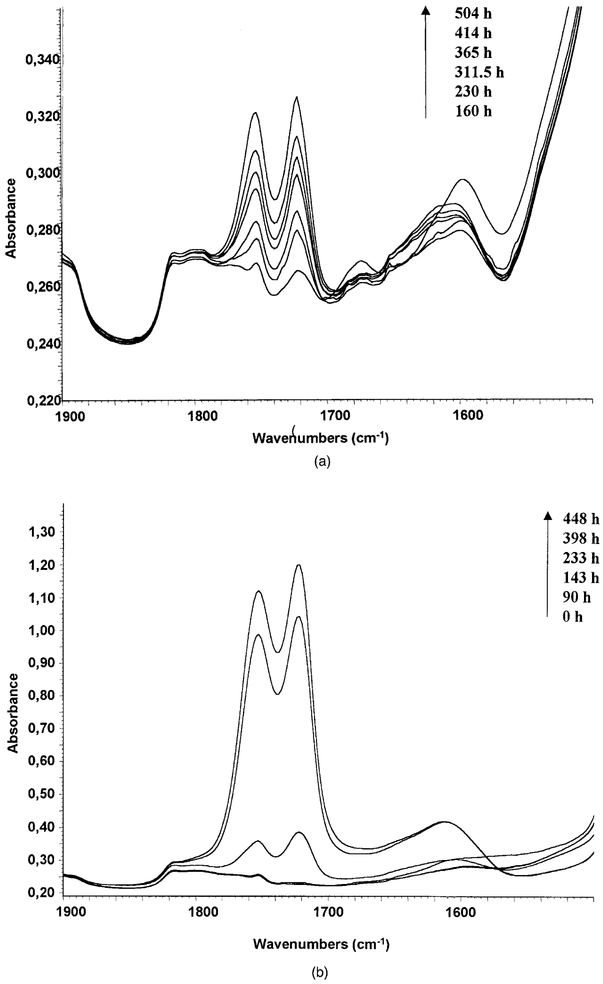


Fig. 5. Evolution of absorbance at 1725 cm^{-1} as a function of irradiation time for PEO films photooxidised at $\lambda \geq 300$ nm, 35°C. (a) PEOlw. (b) PEOhw.



(a)

(b)

Fig. 6. FTIR spectra of PEO films [PEOlw (top), PEOhw (bottom)] thermooxidised at 50°C.

similar behaviour has already been reported in the case of PTMG [7] and attributed to the fact that the β-scission reaction is less favoured in the case of thermooxidation, leading to a higher amount of ester than formate.

3.5.2. Chemical treatments

The results of SF_4 and NH_3 treatments carried out on thermooxidised PEOhw films are shown in Figs. 7 and 8.

SF_4 treatments for 20 min of the thermooxidised PEOhw samples (Fig. 7) lead to the development of a single absorption band at 1858 cm^{-1} resulting from an acyl fluoride derived from aliphatic acids, whereas the broad band centred at 1610 cm^{-1} completely disappears. In the hydroxyl vibration region, after 20 min of treatment, a significant drop of the –OH absorption bands is observed.

The reaction of ammonia with thermooxidised PEOhw samples leads to an increase of absorbance at 1680 and 1595 cm^{-1} (Fig. 8), respectively, attributed to amide groups and carboxylate ions derived from 'aliphatic' acids. Amides are produced by NH_3 reaction with esters.

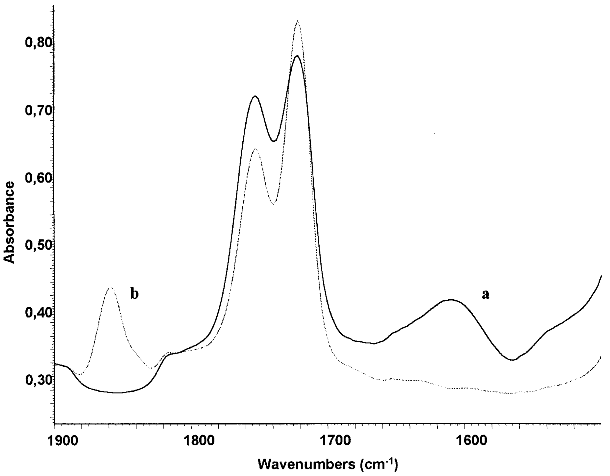


Fig. 7. SF_4 treatment of a PEOhw film thermooxidised at 50°C.

SF_4 treatment gives evidence of the presence of carboxylic acid or carboxylate ions. The IR absorption band at 1610 cm^{-1} might be attributed to formic acid ions. A study of the thermal degradation of PEG with a model molecule (tetraethylene glycol) has already shown the formation of formic acid [26]. In order to identify this absorption band, an appropriate chemical treatment with formic acid was performed on non-irradiated PEOlw and PEOhw films.

3.5.3. Reactivity of molecular formic acid in PEO polymer matrix

Several low molecular weight carboxylic acids (aliphatic, aromatic and substituted acids) have already been introduced into different polymer matrices (such as polypropylene, polyurethane or PVC) and the wavenumbers corresponding to the $\nu_{C=O}$ maxima of the carboxylic acids and carboxylate ions were determined [27]. As concerns inclusion of a molecular carboxylic acid in a polymer film, there is a noticeable influence of the nature of the polymer on the position of those bands.

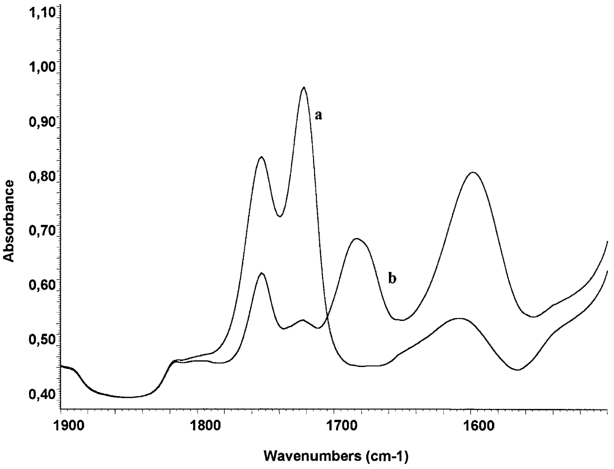


Fig. 8. NH_3 treatment of PEOhw film thermooxidised at 50°C.

Formic acid was introduced by permeation into polymer films. As PEO is a water-soluble polymer, it was not possible to soak the films into an acidic solution. PEO films were exposed to formic acid vapour, at room temperature, in a glass reactor over a concentrated formic acid solution. Reaction time was 1 h.

IR spectra of non-oxidised PEOhw films were recorded before and after exposure to formic acid (Fig. 9a) and to neutralised formic acid with NaOH (Fig. 9b). Same results were obtained with PEOlw films.

Fig. 9 shows the two bands of the carboxylic acids. In PEO polymer matrix, the IR absorption bands of formic acid (Fig. 9a) are centred at 1750 and 1725 cm^{-1}, respectively, for the monomer and the dimer form and a third broad band can be noticed at 1610 cm^{-1}. It was observed that the bands corresponding to formic acid disappear when the samples were stored for a few minutes in the IR spectrometer bench but no modification of the band at 1610 cm^{-1} was observed. The spectra of the films exposed to a neutralised solution of formic acid (Fig. 9b) display mainly an absorption band at 1610 cm^{-1} with a shoulder at 1620 cm^{-1} corresponding to formic acid ions. Traces of formic acid can be noticed.

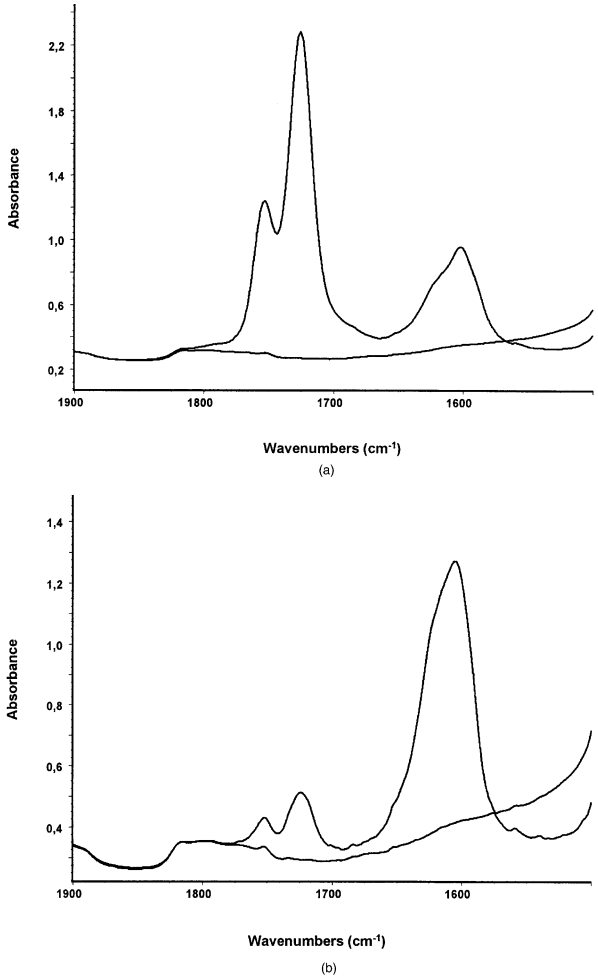


Fig. 9. FTIR spectra of non-irradiated PEOhw films (a) exposed to formic acid (HO–COH) vapour and (b) exposed to neutralised formic acid vapour ($Na^{+-}O$–COH).

These results show that formic acid can diffuse and evaporate from the polymer film, whereas formic acid ions appear to be trapped in the PEO matrix.

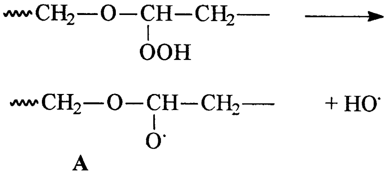
The comparison with the results obtained with molecular formic acid permitted the identification of the chemical structure of the product formed during thermooxidation of PEOhw sample. The band at 1610 cm^{-1} that develops on IR spectra of thermooxidised PEOhw films can be attributed to formic acid ions.

3.6. Degradation mechanism and conclusions

Despite the fact that it does not absorb radiation of wavelengths longer than 300 nm, PEO is very sensitive to photooxidation. The degradation can be initiated by chromophoric impurities which absorb UV light and produce radicals which react further with the polymer [28].

The high photosensitivity of polyethers to UV induced oxidation has been shown to result from the oxidisability of the carbon atoms in the α-position to the oxygen atom [3,5,7,29,30]. The first step of the oxidative reactions is an hydrogen abstraction on the polymeric backbone by a free radical formed by photonic excitation of chromophoric species. Former results obtained in our laboratory [3] have shown that the macroradical produced reacts with oxygen, leading to a peroxy radical that gives an hydroperoxide by abstraction of a labile hydrogen atom.

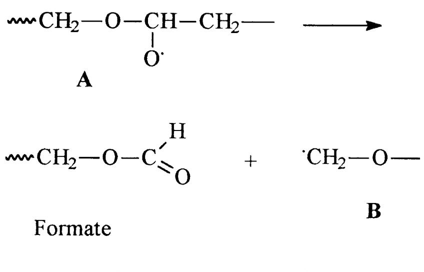
On the basis of the experimental results presented above, one may propose the following mechanism in order to explain the photooxidation of PEO. Photooxidation of PEO leads to the formation of secondary hydroperoxides. The thermal and photochemical decompositions of these hydroperoxides give an alkoxy radical **A**:



$$\sim\sim CH_2-O-\underset{OOH}{\underset{|}{C}H}-CH_2- \longrightarrow \sim\sim CH_2-O-\underset{O^{\cdot}}{\underset{|}{C}H}-CH_2- + HO^{\cdot}$$

A

(1) The main route of evolution of alkoxy radical **A**, as shown in aliphatic polyethers [7–9] is a β-scission which leads to the formation of formate end groups (1725/1185 cm^{-1}) and to macroradical **B**:

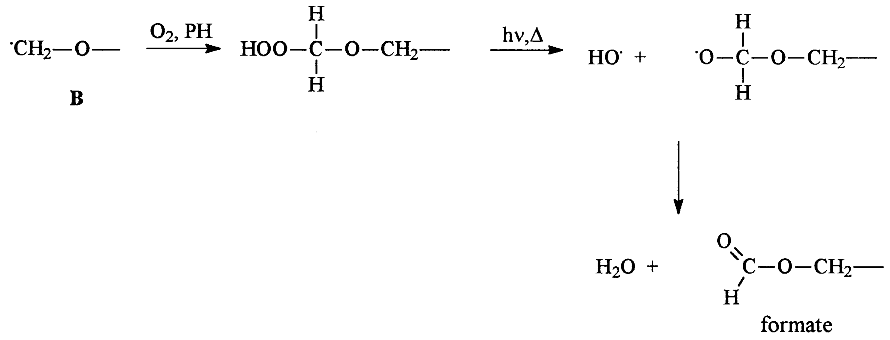


$$\sim\sim CH_2-O-\underset{O^{\cdot}}{\underset{|}{C}H}-CH_2- \longrightarrow \sim\sim CH_2-O-C\overset{H}{\leqslant}O + {}^{\cdot}CH_2-O-$$

A

Formate **B**

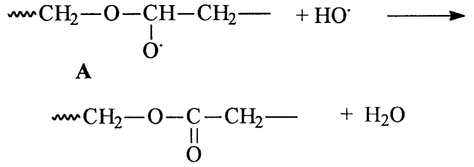
A possible route of decomposition of macroradical **B** is an oxidation leading to primary hydroperoxides. Hydroperoxides can be decomposed to give carboxylic acids either by a direct oxidation [31] or by an oxidation involving the formation of aldehydes [8]. In the case of PEO, the decomposition of these primary hydroperoxides can give formates. This constitutes a supplementary route of formation of formates. By the repetition of this reaction, the chain can be considerably shortened.



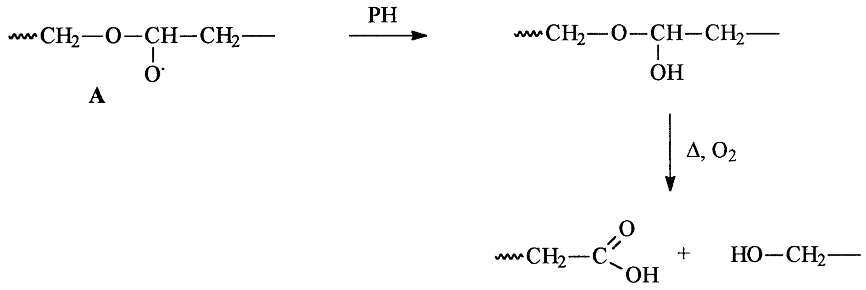
The β-scission of radical **A** could also involve the homolysis of the C–O bonds. However, in this case ketones would be formed. Since no experimental evidence of the formation of such compounds has been obtained, this route may be neglected.

Formates are the most important decomposition products of hydroperoxides formed through chain breaking. Two other ways of reactions of the alkoxy radicals have been reported to occur in the photooxidation of aliphatic polyethers [7].

(2) Cage reaction of the alkoxy radical **A** (with HO˙) may occur, leading to ester functions.



(3) Hydrogen abstraction reaction of radical **A** leads to the formation of a hemiacetal which is thermally unstable and can be decomposed in the matrix to give alcohols and carboxylic acids.



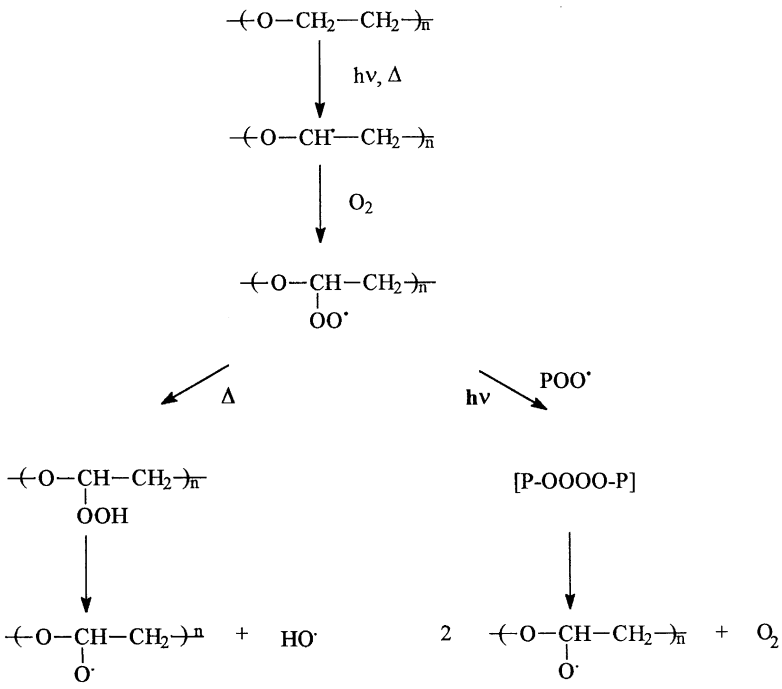
From the shape of the carbonyl band of photooxidised PEO, it is observed that only very weak concentration of carboxylic acids are formed. The oxidation pathway of radical **A** to give a carboxylic acid has then to be considered as minor in photooxidation.

On the contrary, in conditions of thermooxidation, especially in the case of PEOhw, the SF_4 treatment of oxidised samples shows an acyl fluoride, indicating that carboxylic acids were formed. These acidic functions can be attributed to formic acid ions. By comparison of the reactivity of the oxidised polymer with NH_3 that produces besides amide functions also carboxylate ones by hydrolysis, we can assume that formic acid ions might come from partial hydrolysis of formate end group in the polymer matrix.

Besides the mechanism which describes the formation of the oxidation photoproducts by decomposition of hydroperoxides, several authors propose that the formation of the products could result from recombination of alkylperoxy radicals following a Russel type mechanism [32]. In the case of photooxidation of isotactic polypropylene, an alternative mechanism has been proposed [33]. A bimolecular reaction of alkylperoxy radicals can occur:

$$2POO^{\cdot} \rightarrow [POOOOP]$$

The tetroxide intermediate can decompose to give molecular oxygen and alkoxy radicals [34]. Hydroxyl radicals HO˙ are not generated through this reaction. However, in the case of thermooxidation, recent results have shown that this route



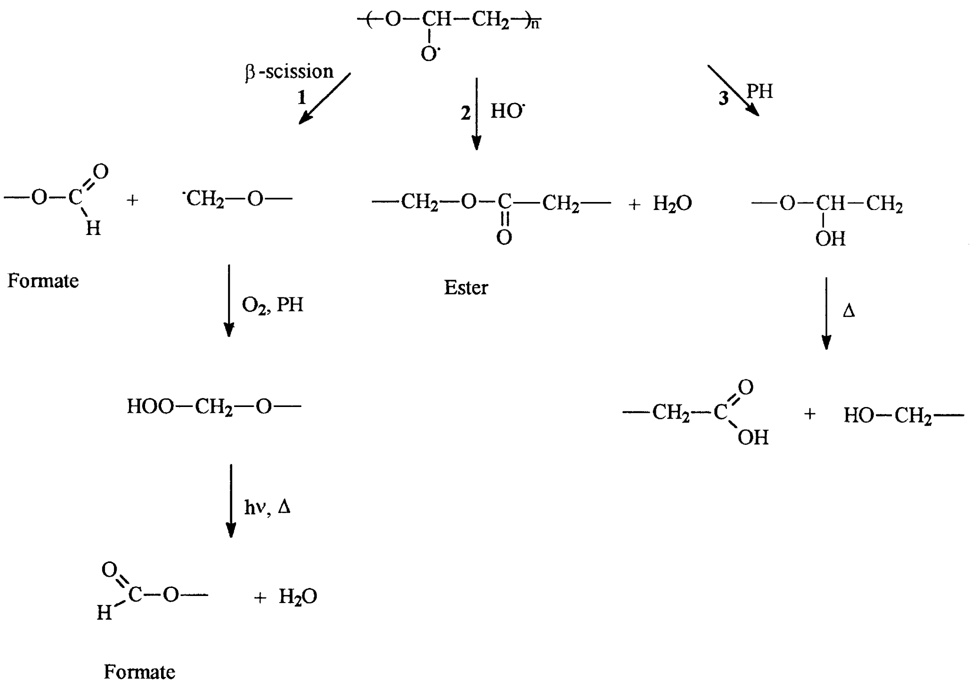
Scheme 1.

could be neglected because no oxygen formation was detected by mass spectrometry analysis of the thermo-oxidation of polypropylene [35].

In the case of PEO, the mechanism involving tetroxide intermediates would be the main route in the case of photooxidation, leading mainly to formates, whereas the thermooxidation would favour the mechanism involving a decomposition of hydroperoxides that leads to macromolecular esters by a cage reaction. This interpretation of the experimental results could be extended to the case of the other polyethers previously studied [5–7,9,11,12].

4. Conclusions

The photochemical evolution of PEO is described as



Scheme 2.

involving a succession of reactions which can occur in a concerted manner. These reactions may be summarised by Schemes 1 and 2.

This study has shown that PEO is very sensitive towards oxidation which takes place on the carbon atom in α-position to the oxygen atom. The hydroperoxides formed react thermally or photochemically to yield several products that have been identified.

The route that involves the formation of hydroperoxides as primary products is favoured in conditions of thermooxidation whereas in conditions of photooxidation recombination of peroxy radicals is more likely to occur. Decomposition of hydroperoxide and tetroxide intermediates leads to the formation of the same macroalkoxy radicals. In photooxidative conditions, the main route of decomposition of the macroalkoxy radicals is a β-scission, which generates formates in a ratio of 5/1 against chain esters. On the contrary, in thermooxidative conditions, hydroxy radicals $HO^{\cdot}$ are formed by decomposition of the hydroperoxides. These hydroxy radicals can react with the macroalkoxy radicals in a cage reaction, producing esters. A same amount of esters and formates is observed in these conditions.

The chain is rapidly damaged as the major carbonylated products are formate end groups. Whereas photooxidation of both PEO samples does not really show a molecular weight effect, thermooxidation gives evidence of a different behaviour for PEOhw which leads to the formation of carboxylic acids.

The next step of our study of PEO deals with the photodegradation of aqueous solutions of PEO in order to identify the photoproducts and the mechanism involved when such a water-soluble polymer is discarded in the aquatic medium and will be submitted to ageing in natural weathering conditions.

References

[1] Molyneux P. Water-soluble synthetic polymers: properties and behavior. Boca Raton: CRC Press, 1983 (chap. 2).
[2] Swift G. Polym Degrad Stab 1998;59:19–24.
[3] Gardette JL, Mailhot B, Posada F, Rivaton A, Wilhelm C. Macromol Symp 1999;143:95–109.
[4] Tabianka M, Philippart JL, Gardette JL. Polym Degrad Stab 1985;12:349–62.
[5] Gauvin P, Philippart JL, Lemaire J. Makromol Chem 1985;186:1167–80.
[6] Gauvin P, Lemaire J. Makromol Chem 1987;188:971–86.
[7] Gauvin P, Lemaire J. Makromol Chem 1987;188:1815–24.
[8] Wilhem C, Gardette JL. Polymer 1998;39:5973–80.
[9] Posada F, Philippart JL, Kappler P, Gardette JL. Polym Degrad Stab 1996;53:19–31.
[10] Mailhot B, Morlat S, Gardette JL. Polymer 2000;41(6):1981–8.
[11] Mailhot B, Morel S, Gardette JL. Polym Degrad Stab 1998;62:117–26.
[12] Gardette JL, Posada F, Philippart JL, Kappler P. Macromol Symp 1997;115:53–67.
[13] Cameron GG, Ingram MD, Qureshi MY, Gearing HM, Costa L, Camino G. Eur Polym J 1989;25(7/8):779–84.
[14] Costa L, Gad AM, Camino G, Cameron GG, Qureshi MY. Macromolecules 1992;25:5512–8.
[15] Costa L, Camino G, Luda MP, Cameron GG, Qureshi MY. Polym Degrad Stab 1995;48:325–31.
[16] Costa L, Camino G, Luda MP, Cameron GG, Qureshi MY. Polym Degrad Stab 1996;53:301–10.
[17] Costa L, Camino G, Luda MP, Cameron GG, Qureshi MY. Polym Degrad Stab 1998;62:49–56.
[18] Costa L, Gad AM, Camino G, Cameron GG, Ingram MD, Qureshi MY. In: Scrosati B, editor. Proceedings of the 2nd International Symposium on Polymer Electrolytes. London: Elsevier, 1990. p. 49–59.
[19] Philippart JL, Sinturel C, Gardette JL. Polym Degrad Stab 1997;58:261–8.
[20] Yoshihara T, Tadokoro H, Murahashi S. J Chem Phys 1964;41(9):2902–10.
[21] Miyazawa T, Fukushima K, Ideguchi Y. J Chem Phys 1962;37(12):2764–76.
[22] Gauvin P, Lemaire J. Makromol Chem 1987;188:971–86.
[23] Gardette JL, Posada F, Philippart JL, Kappler P. Macromol Symp 1997;115:53–67.
[24] Gardette JL. In: Hamid SH, editor. Handbook of polymer science. NY: Marcel Dekker, 2000. p. 671–98.
[25] Kaminska A, Kaczmarek H, Kowalonek J. Polymer 1999;40:5781–91.
[26] Glastrup J. Polym Degrad Stab 1996;52:217–22.
[27] Wilhelm C, Gardette JL. J Appl Polym Sci 1994;51:1411–20.
[28] Rabek JF. Photodegradation of polymers. Berlin/Heidelberg: Springer, 1996.
[29] Posada F, Philippart JL, Kappler P, Gardette JL. Polym Degrad Stab 1995;50:141–58.
[30] Howard JA, Ingold KU. J Chem 1969;47:3797.
[31] Lacoste J, Carlsson DJ. J Polym Sci, Part A: Polym Chem 1992;30:493–500.
[32] Celina M, George GA. Polym Degrad Stab 1993;40:323–35.
[33] Philippart JL, Gardette JL. Polym Degrad Stab 2001;71:189–94.
[34] Russel GA. J Am Chem Soc 1957;79:3871–7.
[35] Philippart JL, Gardette JL. Polym Degrad Stab 2001, submitted for publication.