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Photochemical degradation of poly(ethylene terephthalate)-modified copolymer

T. Grossetête[a], A. Rivaton[a,*], J.L. Gardette[a], C.E. Hoyle[b], M. Ziemer[b], D.R. Fagerburg[c], H. Clauberg[c]

[a]Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS 6505, Université Blaise Pascal, Clermont-Ferrand, F-63177 Aubiere Cedex, France
[b]Department of Polymer Science, University of Southern Mississippi, Hattiesburg, MS 39406-0076, USA
[c]Eastman Chemical Co., Kingsport, TN, USA

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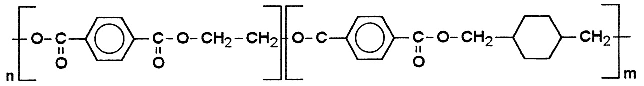
Abstract

The photolysis and the photooxidation of poly(ethylene terephthalate, PET)-modified copolymer have been investigated. The copolymer (COP) that results from the polycondensation of terephthalic acid, ethyleneglycol and 1,4-cyclohexanedimethanol was studied and a comparison with the behaviour of PET was made. Under vacuum irradiation at $\lambda > 300$ nm, the pure photolytic processes involve Norrish type I and II reactions. The formation of the hydroxylated and carbonyl containing photolytic products, which involves hydrogen abstraction from the polymeric backbone, is enhanced in the COP: this result is related to the labile hydrogen atom on the tertiary carbon atom of the cyclohexane units. The pure photolytic processes, in the presence of oxygen, induces oxidation of the aliphatic sequences under polychromatic ($\lambda > 300$ nm) and monochromatic irradiations (254 and 365 nm). The tertiary carbon atoms of the cyclohexane units are shown to be more oxidizable than the methylene groups in the α-position of the ester groups. The decomposition of the hydroperoxides so formed leads to the formation of acetic and formic acids that can migrate out of the film; it also generates hydroxy radicals that is one path leading to the *ortho*-hydroxylation of aromatic rings which gives fluorescence emission to the photooxidised films. The penetration of polychromatic light in the COP sample limits the degradation to the 100 μm top layer. In this superficial layer, chain scission occurs to a large extent as revealed by the identification of terephthalic acid. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate)-modified copolymer; Poly(ethylene terephthalate); Photolysis

1. Introduction

Poly(ethylene terephthalate) (PET) is a material that crystallises slowly at ambient conditions. To avoid such a crystallisation that limits its use, PET-modified copolymer has been synthesised. The copolymer (COP) results from the polycondensation of terephthalic acid, ethyleneglycol and 1,4-cyclohexanedimethanol as shown below:



The photo ageing of PET [1–8], reported to be similar to that of poly(butylene terephthalate) (PBT) [9–11], has been the centre of some interest in literature.

Under vacuum exposure, through direct absorption of light by the chromophoric terephthalate groups in the range 300–350 nm, the data from infrared (IR) studies and the analysis of the evolved gases have been interpreted in terms of Norrish type I and II reactions occurring at the ester bond [1–11]. The radicals generated by the various processes may either react separately through hydrogen abstraction or recombine in coloured conjugated species. Hydrogen abstraction atoms from neighboring molecules leads to the formation of benzoic acid, benzaldehyde, aliphatic alcohol and formate end-group structures. The hydrogen abstraction on the phenyl rings could lead to *meta*-biphenyl groups and could account for one of the recombination pathway.

In the presence of oxygen, the photooxidation of PBT has been shown to involve a complex mechanism in which preponderant photolytic processes and minor photooxidative reactions interfere [10,11]. Primary radicals formed in direct photo-scission processes are able to induce the oxidation of

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* Corresponding author. Tel.: +33-04-73-40-77-43; fax: +33-04-73-40-77-00.
E-mail address: rivaton@mailhost.univ-bpclermont.fr (A. Rivaton).

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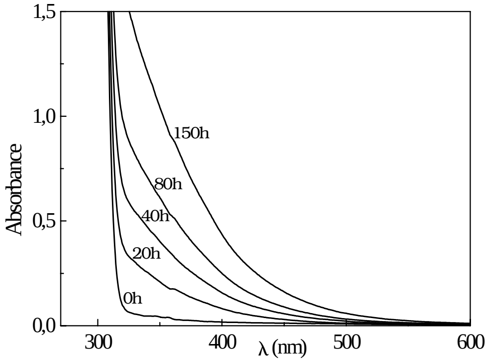


Fig. 1. UV–visible absorption spectra of COP films (50 μm) as a function of UV vacuum exposure ($\lambda > 300$ nm; 60°C).

the methylene groups in the α-position to the ester bond by abstraction of labile hydrogen atoms. Secondary hydroperoxides are formed that accumulate up to a low concentration. The homolysis of their O–O bond leads to the formation of anhydride, esters, aliphatic acids, benzoic acid and aliphatic alcohol as end-groups.

In the present paper, the photolysis and the photooxidation of COP are investigated and compared with that of PET. The identification of the photoproducts—by means of FTIR, UV and fluorescence spectroscopies coupled with derivatisation reactions and physical treatments of irradiated films, mass spectroscopic analysis of the low molecular weight photoproducts and HPLC analysis after solvent extraction—allow us to propose the main photochemical reactions involved in the photodegradation.

2. Experimental

COP was synthesised by conventional methods from dimethyl terephthalate and the requisite diols. PET was supplied by Aldrich. Thick films (50–200 μm) were obtained by compression moulding between PTFE-coated glass cloth at 200 bars for 1 min: at 220°C for COP and at 265°C for PET. To get amorphous polymers, films are immediately quenched in cold water.

Samples were exposed in a SEPAP 12-24 unit (temperature 60°C) for polychromatic irradiations at wavelength longer than 300 nm. This apparatus has been designed for studies of polymer photodegradation in artificial conditions corresponding to a medium acceleration of ageing [10,11]. This unit is equipped with medium-pressure mercury sources (400 W) filtered with a borosilicate envelope that eliminates wavelengths below 300 nm. Irradiations with monochromatic light at 254 and 365 nm were, respectively, carried out in a SEPAP 254 unit and in a SEPAP 365 unit [10,11].

Low temperature thermooxidation experiments were carried out in an aerated oven at 100°C. The macromolecular hydroperoxides formed in the photooxidised samples were titrated using the iodometric method [12].

Irradiated films were exposed to SF_4 (sulphur tetrafluoride) (Fluka) gas at room temperature in an all-Teflon reactor that can be sealed off to allow the reaction to proceed. Carboxylic acids are known to react with SF_4 to give acyl fluorides (RCOF). The acyl fluorides are characterised by a distinct IR absorption band in the range 1810–1845 cm^{-1} [13,14]; the frequency of the maximum of this band is related to the structure of the acid. The SF_4 reaction gives a total disappearance of hydroxyl absorption (alcohols, hydroperoxides). Many aldehydes and ketones are converted to gem-difluoro compounds; esters were monitored to be unreactive under our experimental conditions.

For vacuum photolysis treatments, polymer samples were introduced into pyrex tubes and sealed under vacuum (10^{-6} torr), obtained using a mercury diffusion vacuum line.

UV spectra were recorded on a Perkin–Elmer model 554 equipped with an integrating sphere. A Jobin–Yvon JY3D spectrofluorimeter was used to measure the emission from the polymer film. IR spectra were recorded on a Nicolet 510 FTIR spectrophotometer (nominal resolution of 4 cm^{-1}, 32 scans summation). Measurements of photoproducts profiles in irradiated films were carried out by a technique described earlier [15]. Measurements were performed on a Nicolet 800 equipped with a NICPLAN microscope (liquid nitrogen-cooled MCT detector, 128 scan summations). The films were pressed between two polypropylene plates and were then sliced with a Reichert and Jung microtome. Slices with a thickness of ca 50 μm were obtained and then examined through the FTIR microscope. The spectra were recorded every 10 μm from the irradiated surface towards the core of the sample.

MS analysis of low molecular weight photoproducts trapped in irradiated films were performed using a quadrupolar Balzers type QMG 421 (1–200 amu) mass spectrometer system. High-pressure liquid chromatograms were obtained with a Waters 990 HPLC chromatograph working with a Beckman C18 column and equipped with UV–visible detection. The mobile phase was a methanol (Fisons HPLC solvent)–water mixture with a ratio of 45/55%.

2.1. Photolysis at long wavelengths in vacuum ($\lambda > 300$ nm)

2.1.1. Analysis of the changes of the solid matrix

Irradiation of COP and PET in vacuum at $\lambda > 300$ nm in the absence of oxygen leads to very similar changes in the IR and UV–visible spectra of the exposed samples. Fig. 1 shows the effect of vacuum irradiation on the UV–visible absorption spectra of COP. An increase in absorption, that induces the photo-yellowing of irradiated films, occurs without any defined maximum over almost all the 300–500 nm zone. Changes occur in different zones of the IR spectra. The direct spectra and the subtraction of the initial spectrum from the spectra recorded after several irradiation times permit characterisation of these modifications in the different domains:

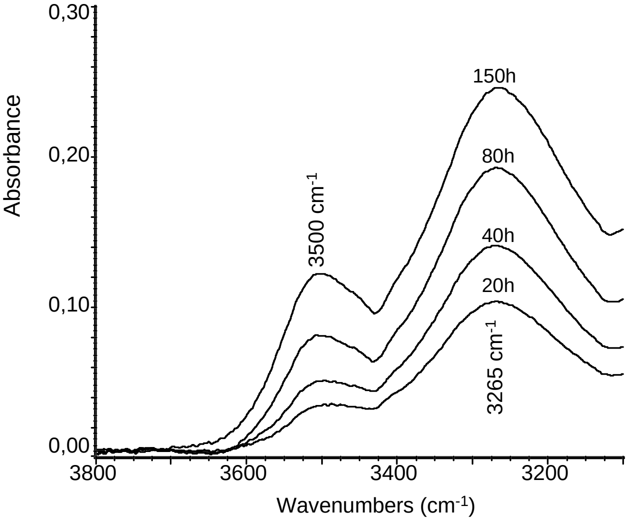


Fig. 2. Subtracted FTIR spectra in the hydroxyl region (difference between the non-irradiated and the irradiated sample) of COP films (50 μm) as a function of UV vacuum exposure.

1. Fig. 2 shows the increase in the hydroxyl absorption for COP. It reveals the formation of two maxima around 3500 and 3265 cm^{-1} that have been, respectively, attributed to the formation of alcohol and acid groups [10,11].
2. In the carbonyl region, a broadening of the initial ester band between 1750 and 1650 cm^{-1} is observed at both extremities. This has been attributed to the formation of benzoic acid end-groups (monomer at 1733 cm^{-1} and dimer at 1696 cm^{-1}) and benzaldehyde end-groups (1702 cm^{-1}). The band at 1650 cm^{-1} can be attributed to double bonds and the one at 1611 cm^{-1} to the modification in ring substitution (*meta*-substituted rings) [10,11].
3. In the region of the C–O stretching vibrations, the band that is observed at 1180 cm^{-1} has been previously attributed to a formate group [10,11].
4. In the region 800–700 cm^{-1}; the thin band that develops at 773 cm^{-1} has been attributed to *meta*-substituted rings [10,11].

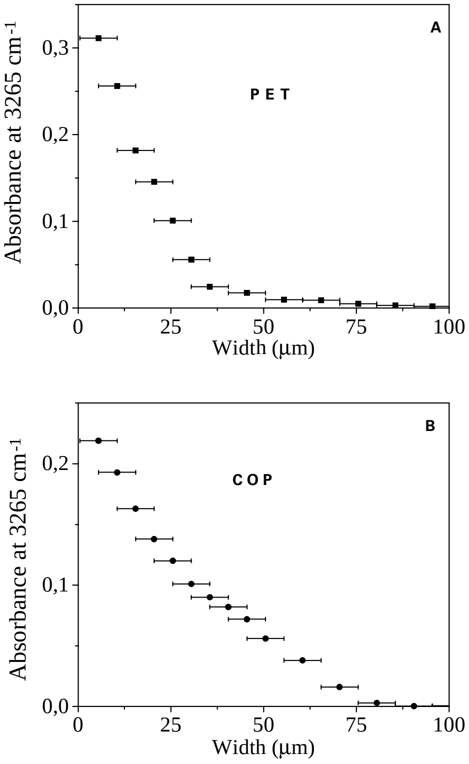


Fig. 3. Photolysis profile measured by micro-FTIR spectroscopy of (A) PET and (B) COP films (200 μm) irradiated in vacuum for 100 h at $\lambda > 300$ nm; 60°C.

2.1.2. Gas phase

Gaseous photoproducts were analysed by mass spectroscopy. CO and CO_2 are found to be the main volatile photoproducts detected as a result of COP and PET vacuum photolysis.

2.1.3. Methanol treatment

Immersion in methanol for 24 h of photolysed films in vacuum leads to some changes of the IR spectra of the so-treated films. In the 3800–3100 cm^{-1} domain, a decrease of the band at 3265 cm^{-1} is observed. The absorption bands that disappear correspond then to molecular products that have been extracted by the solvent.

The UV–visible spectra of the methanol used to extract some of the photolytic products shows two maxima at 240 and 280 nm.

The HPLC analysis of the solvent was carried out and the UV spectra of each fraction were recorded in the range 200–500 nm. Among the various peaks observed, retention time and UV–visible spectra of the most intense peak fit exactly that of terephthalic acid analysed under the same conditions. The generation of terephthalic acid requires chain scission occurring on both sides of terephthalate units.

All the results show that the same products are formed by vacuum photolysis of COP and PET. The cyclohexane units appear then to have no influence on the nature of the photolysis products of terephthalate-type polymers.

2.1.4. Spatial distribution

The photodegradation products were monitored for COP and PET samples irradiated in vacuum for 100 h in the form of 200 μm thick films. The FTIR spectra were recorded every 11 μm from the irradiated surface towards the core of the sample. Fig. 3A and B presents the plots of absorption at 3260 cm^{-1} as a function of the distance from the exposed surface for PET and COP samples.

It is observed that the photolysis of films is predominantly a surface effect: only the 75 μm top layer of COP and the 50 μm top layer of PET show degradation. The subsequent layers of films are unaffected by UV irradiation. The penetration of light in the COP film is more pronounced than in the PET film as the concentration of chromophoric

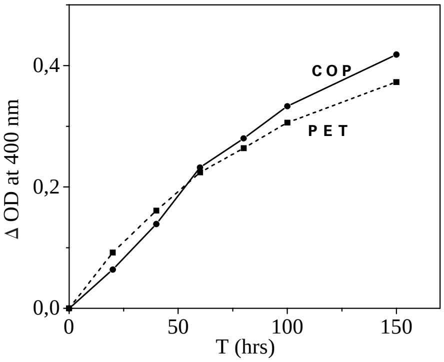


Fig. 4. Increase in the optical density at 400 nm for COP and PET as a function of irradiation time.

aromatic units in COP is only 75% of their concentration in PET due to the presence of cyclohexane units.

2.1.5. Kinetic study of the photolysis

Fig. 4 shows the increase of the optical density at 400 nm for the COP and the PET samples as a function of UV irradiation in vacuum: the yellowing of COP is higher than that of PET. The rate of formation of IR absorbing photoproducts of COP and PET can be compared by plotting the variations of the absorbance at 3465 cm^{-1} as a function of irradiation time.

Fig. 5 shows that the rate of formation of hydroxyl groups is higher in COP; the same observation could be made with carboxyl groups. The difference between COP and PET in the IR range is much more important than the difference observed for the formation of yellowing species.

3. Discussion

These experimental results can be interpreted as follows: the light absorption by the terephthalate chromophoric units extends to around 350 nm. This makes COP, as PET and PBT are, directly accessible to UV light present in terrestrial solar radiation; the shorter wavelengths (300–320 nm) are totally absorbed by COP and PET films with a thickness of 75 and 50 μm, respectively.

As a result of light absorption by the chromophoric terephthalic groups, the two Norrish type I and II mechanisms, as shown in Scheme 1, may occur. The intramolecular Norrish type II process leads to the formation of benzoic acid (1733, 1696 cm^{-1}) and double bonds (1650 cm^{-1}) as end-groups, both observed by FTIR spectroscopy (Scheme 1 Photolysis of COP).

The radicals resulting from the three possible Norrish type I photodissociative reactions may:

- recombine together before or after decomposition through decarbonylation or decarboxylation. CO and CO_2 were found to be the predominant volatile photoproducts detected by mass spectrometry. The various recombination products, for instance benzophenone, are expected to be formed in fairly low concentration and cannot therefore be identified by IR spectrometry; photolysis of these compounds may partially be responsible for the yellow discoloration of the COP and PET films under non-oxidative conditions.
- react separately by hydrogen abstraction of the polymeric backbone. This would lead to the formation of various photoproducts as end-groups observed by FTIR spectroscopy: benzoic acid, benzaldehyde, formate and aliphatic alcohols. The identification of molecular terephthalic acid, that can be extracted from irradiated films by immersion in methanol, is consistent with Norrish type I reactions occurring on both sides of the terephthalate unit followed by hydrogen abstraction processes.

The rate of formation of IR absorbing species is higher in COP than in PET. One explanation of this is due to hydrogen abstraction in COP involving a radical attack on the tertiary carbon of the cyclohexane structure. Evidence that this reaction occurs preferentially to hydrogen abstraction on methylene groups is obtained from the evolution of the FTIR spectra of COP and PET samples irradiated in vacuum (see Fig. 5).

3.1. Photooxidation at long wavelengths ($\lambda > 300$ nm)

3.1.1. Chemical changes in the solid polymers on UV exposure

In the presence of oxygen the irradiation of COP and PET leads to very similar changes in the IR and UV–visible spectra of the exposed samples. The following changes are observed in the IR spectra:

1. In the hydroxyl region (Fig. 6), the appearance of two absorption bands are observed with maxima around 3465 and 3265 cm^{-1}, which account, respectively, for the formation of alcohols and acids. When comparing Figs. 2 and 6, it can be said that relatively similar modifications of the hydroxyl absorbance are observed in vacuum and in air.

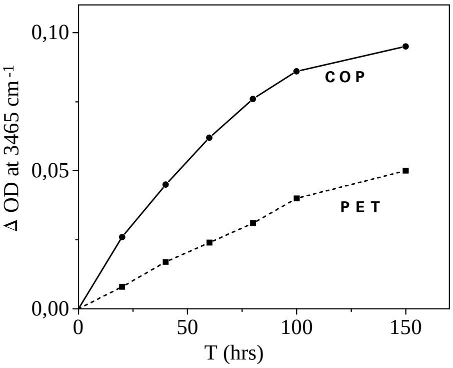
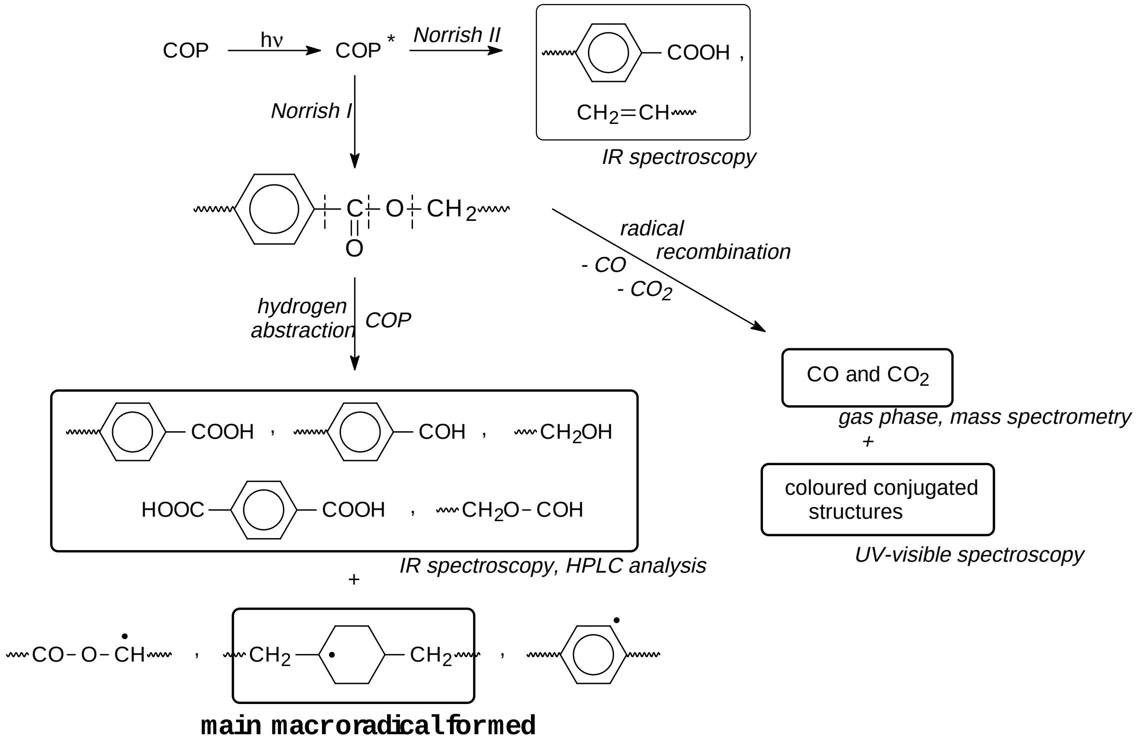


Fig. 5. Increase in the absorbance at 3465 cm^{-1} for COP and PET as a function of irradiation time.



Scheme 1.

2. In the carbonyl region, the strong initial C=O stretching vibration band between 1750 and 1700 cm^{-1} is observed to be enlarged at both extremities. The shoulders that are observed at 1785 and 1611 cm^{-1} have been attributed previously to the formation of anhydrides and to the modification in ring substitution, respectively [10,11].
3. In the region 800–700 cm^{-1} of irradiated COP and PET films, an increase of absorbance is observed with a definite maximum at 773 cm^{-1}, formerly observed throughout vacuum photolysis.

Irradiation of COP (Fig. 7) and PET leads to similar changes of the UV–visible spectra: photooxidation provokes the development of an absorption band with a maximum around 340 nm. The development of this maximum during the photooxidation of PBT has been mainly attributed to the formation of fluorescent monohydroxy-substituted product [10,11].

3.1.2. Measurement of fluorescence

The emission spectra of irradiated films reveal the

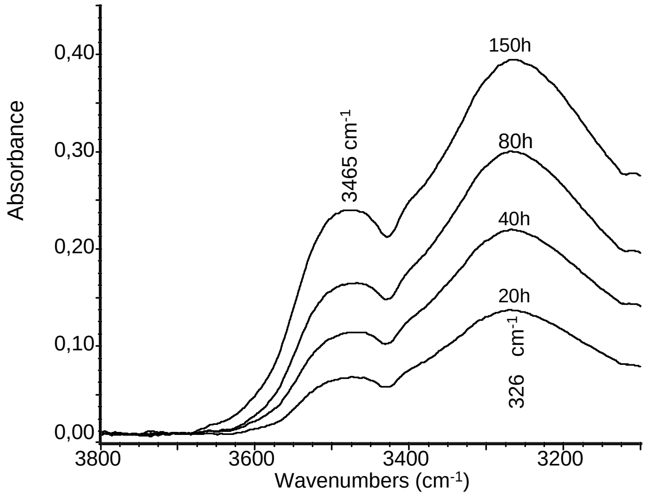


Fig. 6. Subtracted FTIR spectra (difference between the non-irradiated and the irradiated sample) in the hydroxyl region as a function of UV aerated exposure for COP film (50 μm).

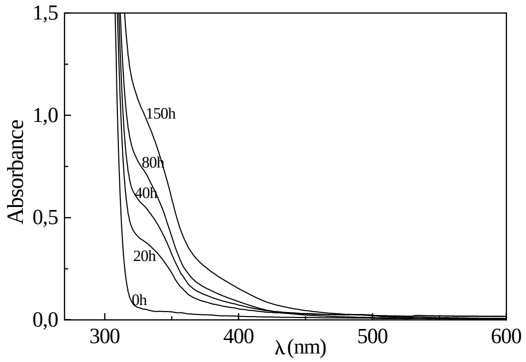


Fig. 7. UV–visible absorption spectra of COP film (50 μm) as a function of UV aerated exposure ($\lambda > 300$ nm; 60°C).

formation of a fluorescent product with a maximum emission wavelength at 460 nm upon excitation at 345 nm. The excitation and emission spectra of this fluorescent material agrees with that found by Pacifici [6] at 459 nm for the monohydroxy-substituted terephthalate compound (excitation at 340 nm). The formation of a second fluorescent compound, as a result of dihydroxy substitution of aromatic rings (excitation at 390 nm, emission at 450 nm [6]), was not observed in this investigation up to 150 h exposure.

It appears then that conclusions similar to those reported above for vacuum photolysis can be given on the basis of the results obtained in photooxidation by means of FTIR, UV–visible and fluorescent spectroscopies: the same evolutions are observed in COP and PET films.

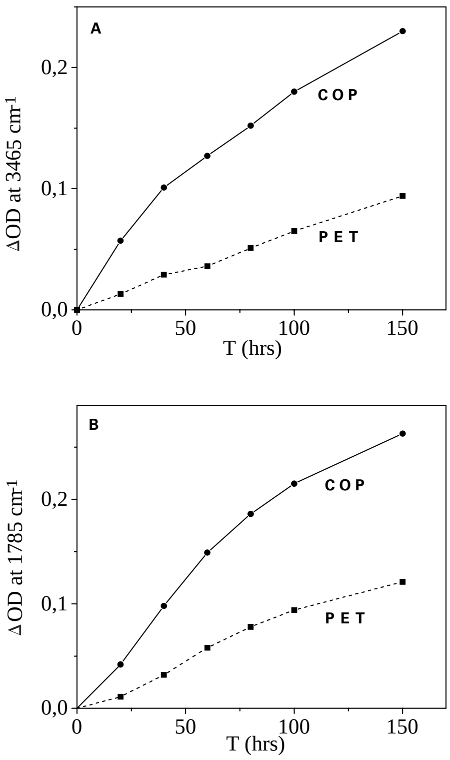


Fig. 8. Increase in the absorbance at (A) 3465 and (B) 1785 cm^{-1} for COP and PET films as a function of irradiation time.

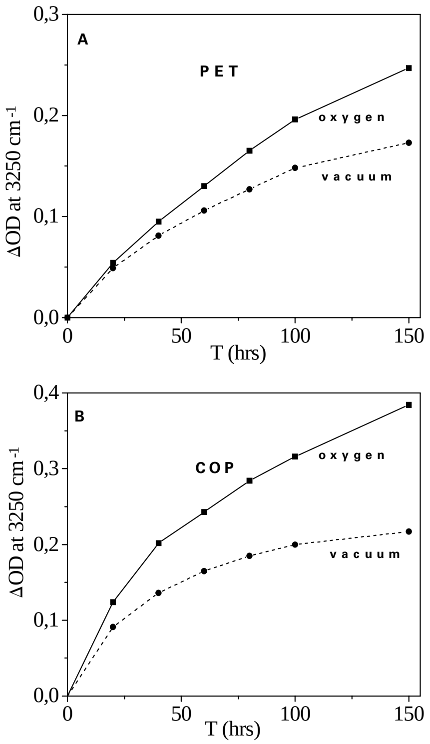


Fig. 9. Increase in the absorbance at 3250 cm^{-1} for (A) PET and (B) COP films, irradiated in the absence and in the presence of oxygen as a function of irradiation time.

3.1.3. Kinetic study of the photooxidation

Fig. 8A and B shows the variations of absorbance at 3465 cm^{-1} (alcohol) and at 1785 cm^{-1} (anhydride) as a function of UV irradiation time. It is clear that the rate of photooxidation is higher for COP than PET.

Hydrogen abstraction is generally considered as the first step involved in the mechanism of photooxidation of polymers. Photolysis experiments have shown that hydrogen atoms on the tertiary carbon of cyclohexane units are considerably more labile than those on the methylene groups in the α-position to ester bonds. As a consequence, the cyclohexane units are anticipated to be more oxidizable than the methylene groups of ethylene glycol. The oxidation of the tertiary carbon atoms of the cyclohexane units of COP is a possible explanation of the formation of prevalent photoproducts in the experiment.

The rates of formation of the acidic photoproducts (measured by the increase of absorbance at 3265 cm^{-1}) under irradiation at $\lambda > 300$ nm in the absence and in the presence of oxygen are reported in Fig. 9A and B. The formation of such acidic groups proves unambiguously that, in the presence of oxygen, direct photolytic processes initially occur which in turn induce the oxidation of the irradiated polymers.

Figs. 10 and 11 show the increase in the fluorescence emission at 460 nm (excitation at 345 nm) and the variation of absorbance at 340 nm, respectively, as a function of UV irradiation time.

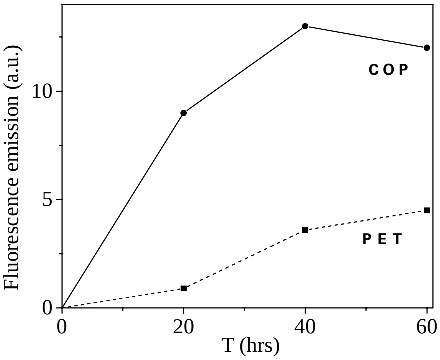


Fig. 10. Increase in the fluorescence emission (arbitrary units) at 460 nm (excitation at 345 nm) for COP and PET films as a function of irradiation time.

The rate of formation of the fluorescent material (Fig. 10) is found to follow the same trend as those observed for the other changes measured in the IR domain (Fig. 8A and B).

The interpretation of Fig. 11 is more complex. It indicates that the development of the absorption band at 340 nm in COP is relatively similar to that of PET. If one assumes that the quantum yield of fluorescence is independent of the chemical structure of the polymer, it could be anticipated that two photoproducts are responsible for the development of the absorption at 340 nm; the contribution of the monohydroxy-substituted product to the development of the UV band would be quite weak.

3.1.4. Depth of photodegradation

Thick films (200 μm) of COP and PET were irradiated for 100 h and the oxidation profiles were determined by recording the spectra every 11 μm. The increase of absorbance in the hydroxyl range was measured and plotted (Fig. 12A and B) as a function of the distance from the exposed face. The oxidation photoproducts appear to be distributed heterogeneously in the COP and PET samples: only the top layers of films are affected by UV irradiation.

The fact that oxidation is confined to the first layers is related to the strong light absorption by the samples: degradation profiles exhibit indeed the same shape under vacuum and aerated exposure.

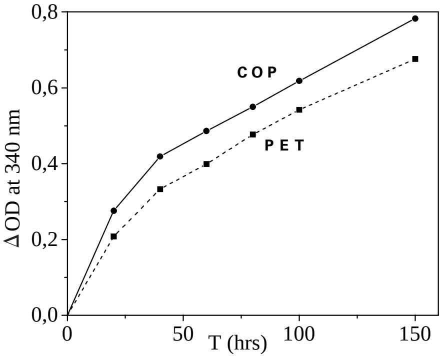


Fig. 11. Increase in the optical density at 340 nm for COP and PET films as a function of irradiation time.

3.1.5. Hydroperoxides titrations

Fig. 13 shows the results of the chemical titration of hydroperoxides for COP and PET films (thickness 50 μm) irradiated in the SEPAP 12-24 unit at 60°C.

The hydroperoxides concentration is higher for COP films than for PET films; such a result is in good agreement with the rate of photooxidation of the two polymers and with the intensity of the fluorescence emission. Hydroperoxides result from the oxidation of macro-alkoxy-radicals formed after hydrogen abstraction. This attack therefore is enhanced on the tertiary carbon atoms of the cyclohexane units. The homolysis of the hydroperoxides provides hydroxyl radicals capable of substitution on the phenyl rings and enhances formation of the fluorescent monohydroxy-substituted terephthalate groups in the polymer. Higher hydroperoxides concentration is linked to the higher intensity in the fluorescence emission at 460 nm obtained for COP. It is reasonable to assume that at least some of the enhanced fluorescence at 460 nm may arise from the decomposition of the hydroperoxides that then results in formation of fluorescent products, although other direct methods of production of labile hydroxy groups may be operative.

3.1.6. Chemical treatments of photooxidised samples

Derivatisation reactions have been carried out to identify the oxidation photoproducts whose formation is observed in the carbonyl region of the IR spectrum. These reactions are carried out by treating photooxidised samples with SF_4 gaseous reactant. Derivatives formed by reaction of aliphatic and aromatic carboxylic acids with SF_4 are characterised by a distinct C=O absorption [13,14].

SF_4 treatment of irradiated COP and PET films shows the development of an intense absorption band at 1816 cm^{-1} and a weak band at 1841 cm^{-1}. This behaviour reveals the presence of aromatic acids (1816 cm^{-1}) and of aliphatic acids (1841 cm^{-1}), respectively, with lesser amounts of the aliphatic acids. Results of SF_4 treatments of COP and PET films throughout irradiation are shown in Fig. 14A and B.

The rate of oxidation of COP is higher than that of PET. The distribution between aliphatic and aromatic acids of carboxylic photoproduct resulting from this oxidation deduced by means of chemical treatments confirms the results deduced from the analysis of the UV and IR spectra: that the oxidation of the cyclohexane units appears to be the source of much of the aliphatic carboxylic acids formed.

3.1.7. Analysis of the volatile products

3.1.7.1. Thermolysis of photooxidised samples COP and PET films photooxidised for 100 h were subjected to thermolysis at 100°C in the absence of oxygen. A fairly weak decrease of the absorbance is observed in the hydroxyl

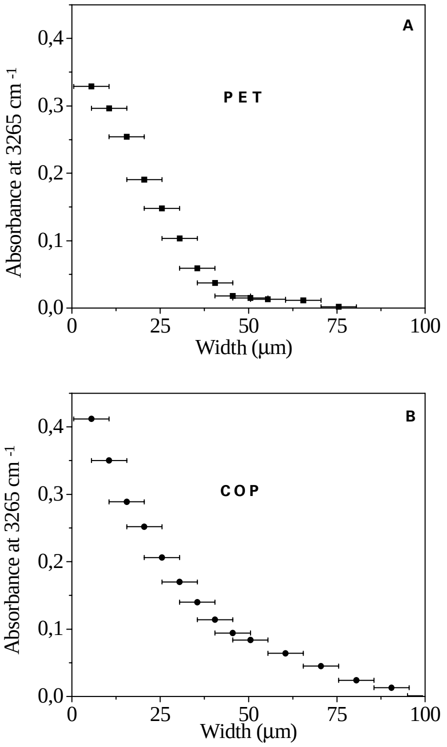


Fig. 12. Photooxidation profile measured by micro-FTIR spectroscopy of (A) PET and (B) COP films (200 μm) irradiated in the presence of oxygen for 100 h at $\lambda > 300$ nm; 60°C.

region of the COP film. Treatments by SF_4 carried out after thermolysis revealed that the intensity of the acyl fluoride band at 1841 cm^{-1} decreased by 12% throughout thermolysis of COP film; in PET film, thermolysis was found to have no effect on the concentration of the aliphatic fluoride band. In both polymers, the intensity of the aromatic acyl fluoride band at 1816 cm^{-1} was shown to be invariant throughout thermolysis.

It can be concluded that about 12% of the aliphatic acid groups are lower molecular weight compounds that can be lost by evaporation from the COP film under heating at 100°C.

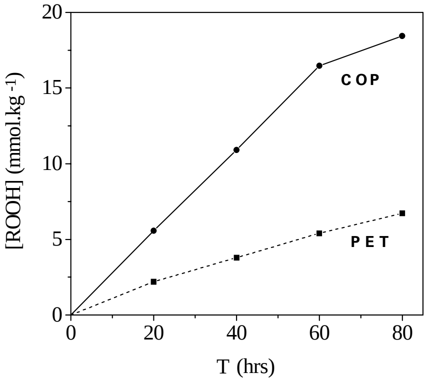


Fig. 13. Hydroperoxidic groups concentration as a function of irradiation time in COP and PET films (50 μm) photooxidised at $\lambda > 300$ nm; 60°C.

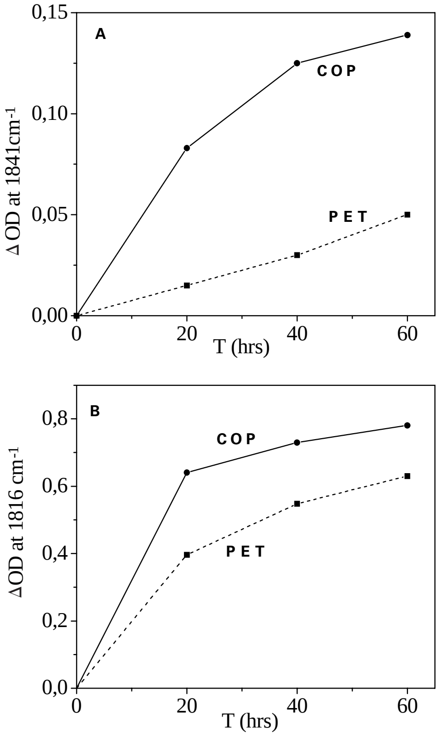


Fig. 14. Increase in the absorbance at (A) 1841 and (B) 1816 cm^{-1} in COP and PET films pre-irradiated at $\lambda > 300$ nm after SF_4 treatment as a function of irradiation time.

3.1.7.2. Analysis by mass spectroscopy Samples of polymer were introduced in an irradiation cell and the cell was filled with oxygen and sealed during irradiation. After irradiation, the cell is connected to a mass spectrometer apparatus. After complete removal of oxygen present in the cell, one observes the formation of carbon monoxide and carbon dioxide as in the photolysis experiment. The mass spectrum of both polymers also reveals the formation of water.

The other volatile products are then removed from the cell by pumping off the gas phase and the cell is progressively warmed up to 100°C. In the case of COP only, the mass spectum reveals the presence of acetic acid ($m/e = 15$, 43, 45, 60) and formic acid ($m/e = 29$, 44, 45, 46); comparison with the mass spectra of selected products confirm this identification. In the case of PET, the mass spectrum reveals no trace of carboxylic acid.

The analysis of the gas phase appears to be in good accordance with SF_4 treatments. The oxidation of the cyclohexane units results in the formation of saturated carboxylic acids: acids that terminate chains as well as acetic acid and formic acid that can migrate out of the polymer matrix.

3.1.8. Analysis of the extractable photoproducts

3.1.8.1. Analysis of the films after immersion in methanol Immersion in methanol for 24 h of photooxidised

Table 1
Influence of methanolic treatment on the intensity of the acyl fluoride bands after SF_4 treatment

	Intensity of the band at 1841 cm^{-1} (aliphatic acid)	Intensity of the band at 1816 cm^{-1} (aromatic acid)
COP photooxidised 100 h	0.120	0.48
COP photooxidised 100 h and immersed 24 h in MeOH	0.061	0.17
PET photooxidised 100 h	0.063	0.54
PET photooxidised 100 h and immersed 24 h in MeOH	0.019	0.16

films leads to some changes in the IR and UV–visible spectra of the so-treated films. In the whole range of the IR investigations (hydroxyl and carbonyl ranges), a decrease of the bands attributed to the photooxidation products is observed: the concentration of molecular photoproducts extracted by the solvent was observed to be more important in COP films than in PET films. In the UV–visible range, a slight decrease in the intensity of the absorption band at 340 nm is observed on the spectra of both polymers.

Treatments by SF_4 carried out after immersion in methanol reveal that the intensity of the acyl fluoride bands at 1841 and 1816 cm^{-1} is lowered by the methanolic treatment as shown in Table 1.

One may conclude that the carboxylic acid groups that accumulate in COP and PET films include acid-terminated chains and low molecular weight carboxylic acids.

3.1.8.2. Analysis of the methanolic solution The UV–visible spectra of the methanol used to extract the photooxidation products shows maxima at 240 and 280 nm (like with vacuum photolysed films) and at 340 nm. Measurement of the fluorescence of the methanolic solution reveals the presence of a fluorescing product at 450 nm (excitation at 340 nm).

The UV and emission spectra of the methanolic solution indicate that some of the low molecular weight products are monohydroxyterephthalate groups.

The chromatogram of the methanol used to extract the photooxidation products reveals some analogy with the chromatogram of the methanol used to extract the oxidation products. Among the extracted products, retention time and UV–visible spectra of the most intense peak was fit exactly with terephthalic acid, as observed with photolysed films.

The identification of salicylic acid, when irradiation is carried out in the presence of oxygen, supports the monohydroxylation of terephthalate units.

3.2. Influence of the excitation wavelength

It was shown that, under polychromatic irradiation at $\lambda > 300$ nm, the photooxidation of PBT involves a complex mechanism of both photolysis and photooxidation. To obtain a more detailed understanding of the various reactions involved in the photodegradation of COP, the probabilities of direct phototransformation and photooxidation were modified through the variation of the excitation wavelength of the polymer.

1. Under short wavelength exposure ($\lambda = 254$ nm), the incident radiation is totally absorbed by the aromatic chromophores groups located in the first 5 μm layer of the irradiated film. Such an excitation involves pure photolytic processes.
2. Under long wavelength exposure ($\lambda = 365$ nm), the absorption of the incident radiation by the aromatic polymers, and therefore, the extent of direct photolytic processes is fairly low through the whole volume of the 50 μm exposed films.

The evolution of the IR and UV–visible spectra of COP and PET films irradiated at 254 and 365 nm are relatively similar to those reported above for polychromatic irradiation at($\lambda > 300$ nm : the same photoproducts are formed under both conditions.

The main discrepancy observed between short wavelength irradiation ($\lambda = 254$ nm) and longer wavelength exposure ($\lambda > 300$ and $\lambda = 365$ nm) is related to the distribution profile of the photoproducts. Photooxidation at 254 nm occurs in a very superficial layer that is thoroughly oxidised. The analysis of the gas phase under irradiation at 254 nm revealed that the diffusion of formic and acetic acids occurs to a larger extent; and the immersion in methanol of films that have been pre-irradiated at 254 nm showed that most of the oxidation products can be extracted by the solvent.

It is concluded that in the highly oxidised layer of films irradiated at 254 nm, the concentrations of the photoproducts and chain scission reach very high stationary values: most of the observed photoproducts are small molecules.

The extent of the direct phototransformation (increase of the absorbance at 773 cm^{-1}) and the accumulation of the photooxidation products (increase of the absorbance at 1785 cm^{-1}) as a function of irradiation time under exposure at 254 and 365 nm are reported, respectively, in Figs. 15 and 16.

The main comment that can be made about the results in Figs. 15 and 16 is that, whatever the irradiation wavelength

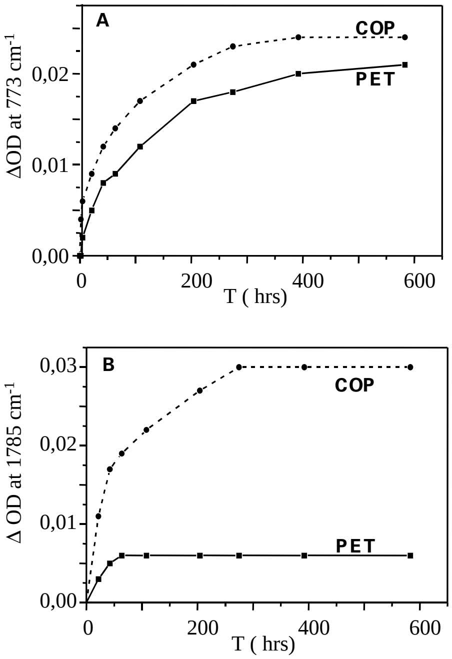


Fig. 15. Increase in the absorbance at (A) 773 and (B) 1785 cm^{-1} for COP and PET as a function of irradiation time under monochromatic exposure at 254 nm.

is, the same mechanisms are involved in the photodegradation of terephthalate polymers:

- In the first steps of irradiation, pure direct photolytic processes are involved in the photooxidation of the polymer films. The rates of photodegradation of COP and PET are similar as only aromatic rings are involved in the initial primary photochemical process.
- As irradiation time increases, the rate of photooxidation of COP is observed to be higher than that of PET. This suggests that the photo-induced oxidation of polyesters occurs at least partially by hydrogen abstraction of the radicals formed in the Norrish type I reaction: the rate of formation of photoproducts that result from the oxidation of the cyclohexane units is higher than the one that results from the oxidation of the methylene groups.

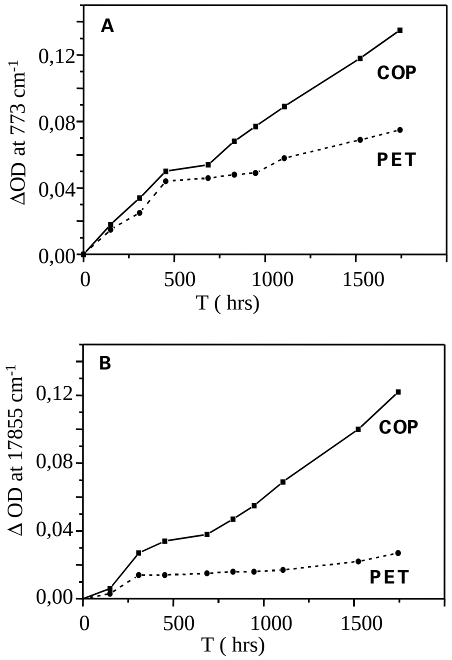


Fig. 16. Increase in the absorbance at (A) 773 and (B) 1785 cm^{-1} for COP and PET as a function of irradiation time under monochromatic exposure at 365 nm.

4. Discussion

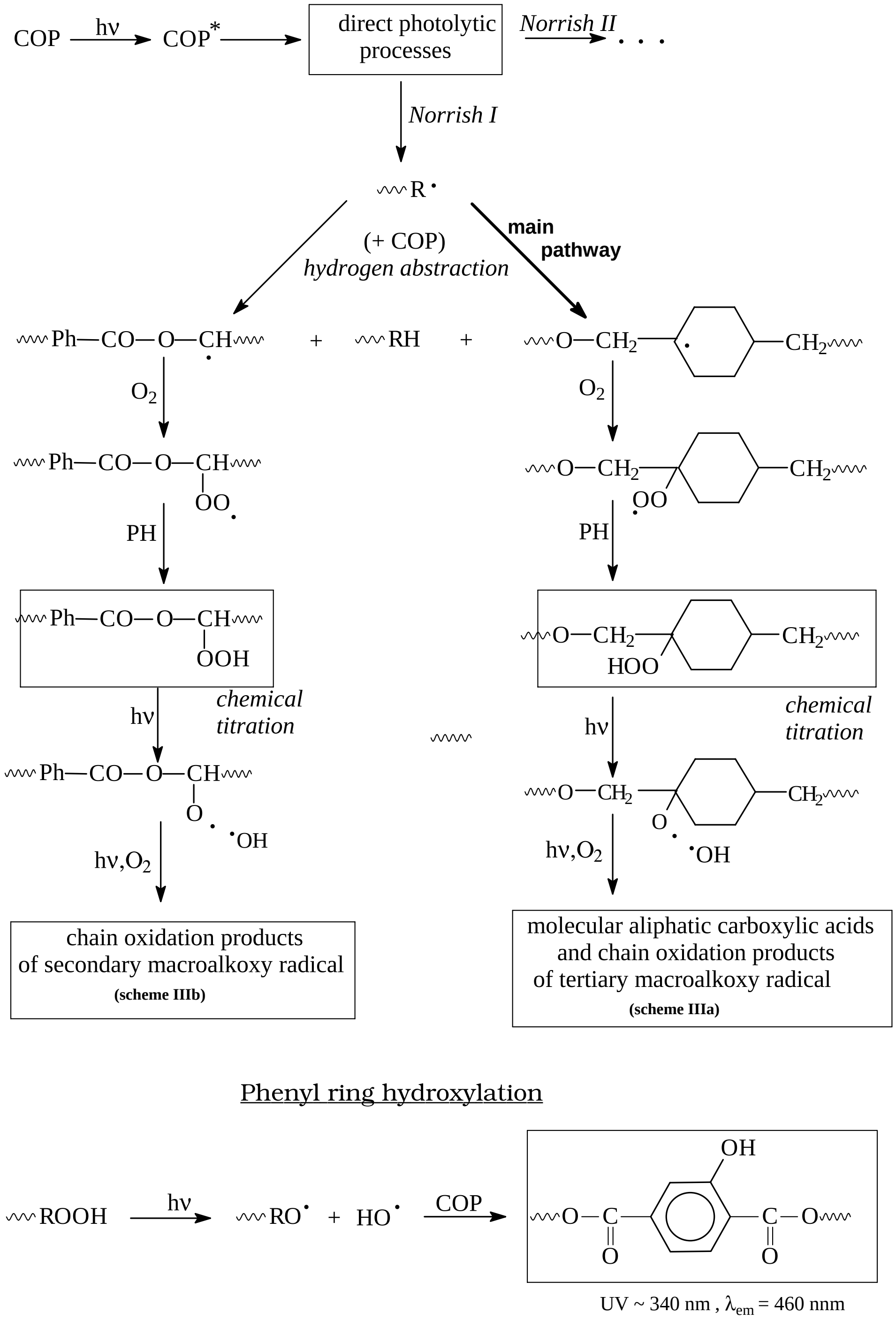
It is well known that the photooxidation of terephthalate-type polymers (PET, PBT) involves a complex mechanism in which preponderant photolytic processes and minor photooxidative reactions interfere [1–11]. Primary macroradicals formed upon direct homolysis of the ester bond are able to induce the oxidation of the polymer through abstraction of the labile hydrogen atoms of the polymeric backbone.

The experimental results given above permit one to conclude that the photooxidation of COP involves analogous processes. When irradiation is carried out in the presence of oxygen, direct photolytic processes initially occur: during short exposure times, the behaviour of the irradiated polymer films is quite similar in the presence and in the absence of oxygen (see Fig. 9) under polychromatic ($\lambda > 300$ nm) and monochromatic irradiation (254 and 365 nm). As irradiation proceeds, the oxidation of aliphatic and aromatic sequences accounts for:

- the increase in the rate of formation of IR absorbing photoproducts (by a factor of 1.5–2);
- the development of an absorption band around 340 nm in the UV range;
- the fluorescence emission;
- the formation of products in the polymer matrix or in the gas phase for the aerated exposure, specifically.

Under polychromatic irradiation at $\lambda > 300\,nm$, the penetration of light in the exposed sample limits these oxidation reactions to the first 100μm. Let us detail such oxidative processes (photooxidation of COP) as reported in Scheme 2.

Hydrogen abstraction by the radical species formed in Norrish type I photodissociative processes can induce the oxidation of the aliphatic sequences. Photolysis experiments have shown that this reaction involves mainly the tertiary carbon atoms of the cyclohexane units rather than the secondary methylene groups: the rate of photooxidation of COP is observed to be higher than that of PET. Subsequent oxygen addition followed by hydrogen abstraction results in the formation of hydroperoxides that can be chemically titrated. The higher total concentration of hydroperoxide groups titrated in COP than in PET seems quite reasonable since cyclohexane units are



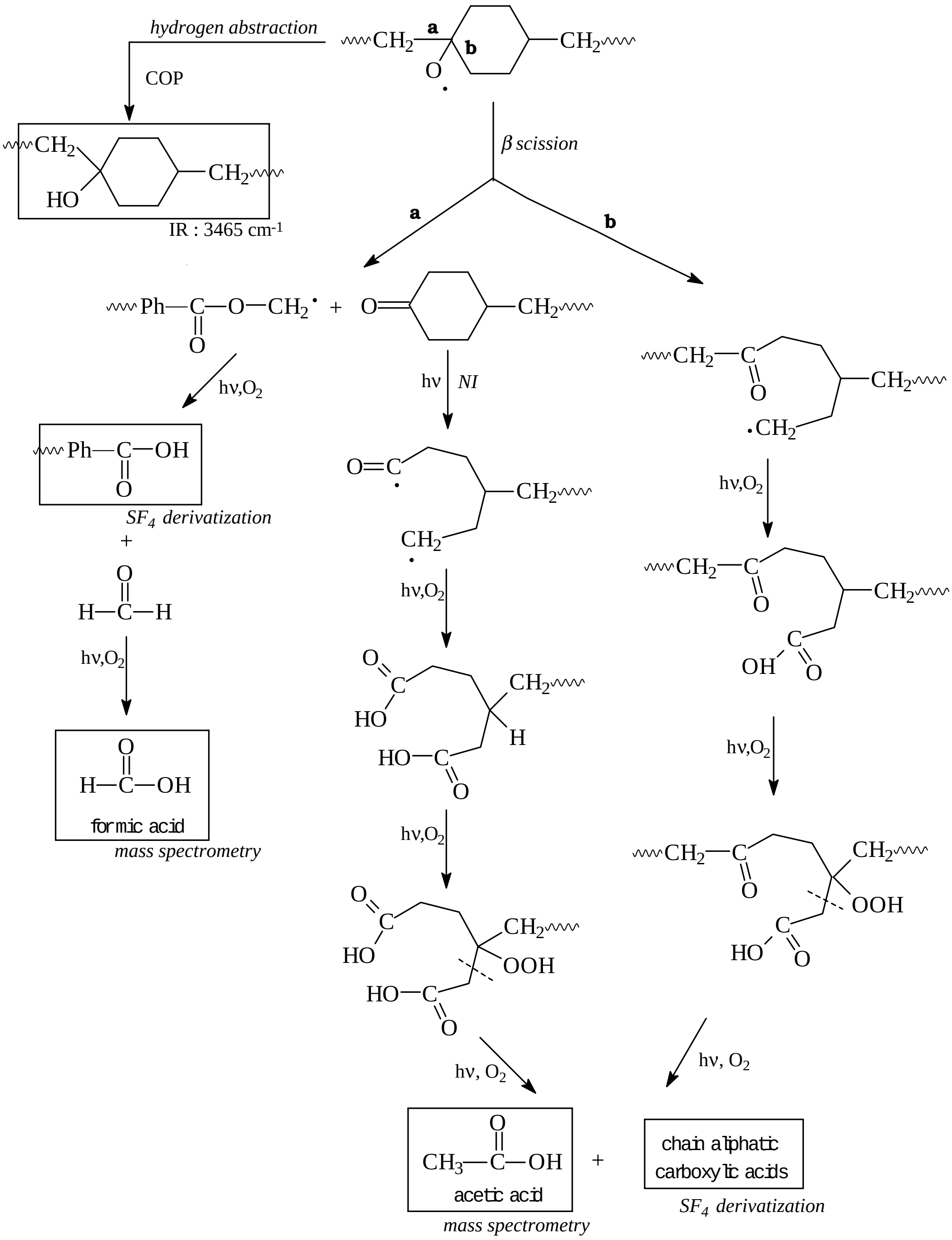
Scheme 2.

more labile than those on secondary methylene groups in the α-position to ester bonds. The relative yields of the Norrish type I cleavage processes in COP and PET films may also contribute to differences in hydroperoxide groups, but no quantitative results have been obtained to date.

The hydroperoxides are photo-unstable and the homolysis of the O–O bond gives alkoxy and hydroxy radicals. The evolution of alkoxy radicals is responsible for the formation of IR absorbing oxidation products; hydroxy radicals are responsible for the formation of fluorescent UV absorbing species.

The tertiary macroalkoxy radical may react in three ways as reported in Scheme 3a (oxidation of tertiary macroalkoxy radicals; formation of molecular carboxylic acids):

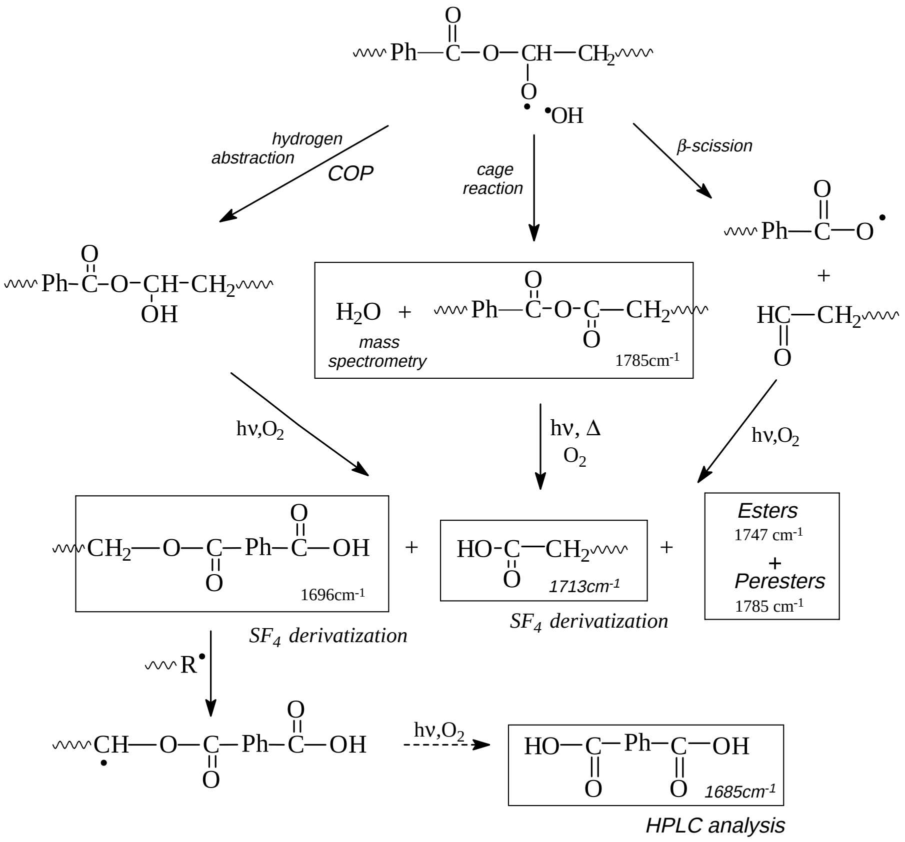
- by abstraction of an hydrogen atom to the polymeric backbone, hydroxyl groups are formed. These hydroxyl



Scheme 3a.

groups contribute to the development of the IR absorption at 3465 cm^{-1} (intermolecularly bonded OH).

- β-scission of the macroalkoxy radical in (a) leads to a cyclohexanone type structure and to a secondary macroradical. Oxidation of this radical leads to two types of carboxylic acids whose formation was evidenced by SF_4 derivatisation: benzoic acid as end-groups and molecular formic acid. This low molecular weight photoproduct can migrate out of the polymer matrix and is detected by analysis of the gas phase. Norrish type I reaction of the cyclohexanone promotes the opening of the aliphatic ring and the formation of two radicals that are oxidised into chain carboxylic acid structures. The oxidation of the other tertiary carbon of the opened aliphatic ring leads finally to end-chain carboxylic acids and acetic acid detected by analysis of the gas phase.
- β-scission of the macroalkoxy radical in (b), implying that the hydroperoxidation of both tertiary carbon atoms leads also to final end-chain carboxylic acids and molecular acetic acid. It was indeed shown (SF_4 derivatisation) that the photooxidation of COP, in comparison



Scheme 3b.

to the one of PET, favours the formation of aliphatic carboxylic acids.

The evolution of the secondary macroalkoxy radical has been previously described in the photooxidation of PBT and PET [9–11]. The alkoxy radicals were shown to be converted into keto-hemiacetals through hydrogen abstraction, into anhydrides through cage reaction involving the formation of H_2O (dectected by mass spectometry analysis of the gas phase), or into aliphatic aldehydes and carboxy radicals through β-scission.

These photoproducts are photo- and thermally-unstable, and the oxidation of carboxy radicals occurs. The detection of the IR bands of photoproducts and/or the characterisation of derivatives of esters, peresters as well as aliphatic and aromatic acids as end-groups permits the proposal of the mechanism (oxidation of secondary macroalkoxy radicals) in Scheme 3b.

The identification of terephthalic acid, after methanolic extraction and HPLC analysis, could involve the oxidation of the two methylene groups on each side of a terephthalate unit. Terephthalic acid can also be made by other non-oxidative routes.

No lower molecular weight aliphatic carboxylic acids are detected in the gas phase of PET; formic acid and acetic acid have to be therefore considered as specific to the oxidation of the cyclohexane unit.

It has been proposed in the literature that either substitution reactions by hydroxy radicals or the direct oxidation of phenyl radicals (obtained after hydrogen abstraction) are capable of leading to the mono- and di-hydroxylation of aromatic rings [16–21]. On the basis of the absorption band at 340 nm, associated with the characterisation of the fluorescence of photo-oxidised films [6], it is proposed that only the mono-hydroxylation of aromatic rings occurs in COP and PET films irradiated up to 150 h in SEPAP 12-24 at 60°C. The absorption band and the fluorescence emission of the dihydroxylated structure [6] were not observed.

The fluorescence emission of the COP film was observed to be significantly higher than that of PET, and the same trend was measured in hydroperoxidic group concentration. As the aromatic rings of COP and PET should be equivalent towards hydroxyl radical substitution, it is proposed that at least in part, the fluorescence of COP and PET photo-oxidised films results in *ortho*-substitution of the aromatic rings by hydroxy radicals produced from the homolysis of hydroperoxides groups. Other sources of hydroxy radicals are also possible as will be discussed in a future paper. The HPLC identification of salicylic acid after methanolic extraction supports the monohydroxylation process.

While the amount of direct absorption of light by the terephthalate polymers is quite different, the same mechanism of photodegradation occurs under both monochromatic irradiation at 254 and 365 nm: the photooxidation of the terephthalate polymers is induced at least partially through abstraction of the labile hydrogen atoms by the macroradicals formed in the direct homolysis of the ester bond. Other oxidative mechanisms may contribute to the formation of the monohydroxy terephthalates and acid structures detected in this investigation.

5. Conclusions

In light of present results and in forthcoming work, we would like to emphasise the following points:

- The Norrish type II reaction leads to the formation of acids and double bonds. We have observed the double bond product of the Norrish type II reaction in the COP samples at 1650 cm^{-1}.
- It is well known that monohydroxy terephthalate absorbs at 340 nm in the UV. We will show in a future publication that another species, benzaldehyde and/or its photooxidation products, is responsible for some of this absorbance.
- Increased cyclohexanedimethanol content produces more photooxidation products.

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