

Photo-oxidation of phenoxy resins at long and short wavelengths—I. Identification of the photoproducts

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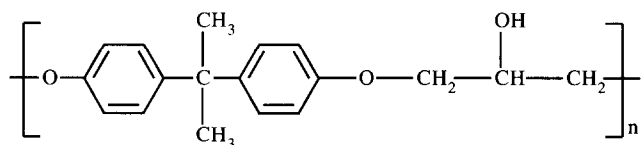
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Phenoxy resin films were exposed to radiation of long wavelengths ($\lambda > 300$ nm) and short wavelength ($\lambda = 254$ nm). The products resulting from the photo-oxidation of phenoxy resin have been identified by means of various techniques such as Fourier transform infra-red spectroscopy and ultraviolet spectrophotometry, chemical derivatization reactions and physical treatments, and mass spectrometry. Results show that phenyl formate end-groups are the main oxidation products that accumulate in films photo-oxidized at long wavelengths; no phenyl formate structures have been found under short-wavelength exposure. © 1997 Elsevier Science Limited

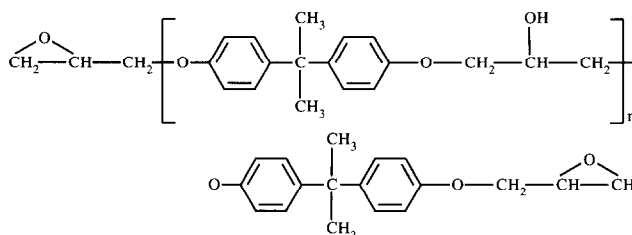
1 INTRODUCTION

Phenoxy resins (PR) are usually treated as being part of the family of epoxy polymers: both are products of the condensation of bisphenol-A [2,2-bis(4'-hydroxyphenyl)propane] with epichlorohydrin (1-chloro-2-3-epoxy propane).

- Phenoxy resins are linear macromolecules with high molecular weight, in the range 30 000 to 70 000. Chain ends are mainly phenolic; the content of epoxy end-groups is fairly low. Because of their high molecular weight, phenoxy resins can be used without further transformation.



- Epoxy resins have a molecular weight in the range up to a few thousand; macromolecular chains are terminated by epoxy groups.



Before use, epoxy resins are transformed into epoxy polymers: curing agents (anhydride or amine) crosslink the resin to form a rigid polymer which has a rather complex structure.

As the repeat units are identical, it is postulated that experimental results obtained with phenoxy resins could be a means to simplify the interpretation of the photo-oxidation of cured epoxy polymers.

There are few references in the literature dealing with the degradation of epoxies. Most of the papers are devoted to the investigation of the chemical structures of commercial polymers.¹⁻⁶ The thermal and photodegradation of epoxy resins has been studied by Grassie *et al.*⁷⁻⁹ The rapid degradation observed was mainly attributed

to the instability of epoxy end-groups that are no longer present in the cured resins.

Kelleher and Gesner studied the photolysis and photo-oxidation of phenoxy resins.¹⁰ The light-induced degradation of the phenoxy polymers was characterized by measurement of the volatile products (CO, CO₂, etc.), the chain scissions and the simultaneous rapid crosslinking reactions and yellowing.

On the basis of published data, one cannot consider the mechanism of photo-oxidation of PR as being established conclusively since the oxidation photoproducts formed in irradiated films have not been identified. Surprisingly, the sensitivity of PR towards photo-oxidation has never been attributed to the polyether structure. In previous works carried out in our research group,^{11–13} it was shown that the photo-oxidation of aliphatic polyethers results from the oxidizability of carbon atoms in the α position to oxygen atoms of the ether groups. Moreover, one must expect a rapid photo-oxidation of PR because the chromophoric units of this aromatic polyether give an absorption in the near-ultraviolet (UV) range that can be presumed to be responsible for direct phototransformation of the polymeric backbone.

In the present paper, we report the identification of the photoproducts produced in PR films exposed to UV-visible light ($\lambda > 300$ nm) and to monochromatic short-wavelength radiation ($\lambda = 254$ nm). The analytical techniques used to identify oxidation products are based on Fourier transform infra-red (FTIR) spectroscopy coupled with derivatization reactions and physical treatments; mass spectrometry (MS) analysis of the gas phase has also been carried out. In the second paper in this series, a general mechanism accounting for the photo-oxidation of PR at $\lambda > 300$ nm and at $\lambda = 254$ nm will be proposed and discussed.

2 EXPERIMENTAL

Films were obtained from a sample of commercial PR (Aldrich). Thin films (10–30 μm) were obtained by evaporation of PR solutions in CHCl₃. Thick films (50–200 μm) were prepared by pressing PR at 200 bar and 190°C for 90 s.

Samples were irradiated in various types of apparatus that have been described previously.¹⁴

- For polychromatic irradiations at wavelength longer than 300 nm, PR films were exposed in a

SEPAP 12-24 unit (temperature 60°C). This apparatus was designed for studies of polymer photodegradation in artificial conditions corresponding to a medium acceleration of ageing. This unit is equipped with medium-pressure mercury sources (400 W) filtered with a borosilicate envelope that eliminates wavelengths below 300 nm.

- A SEPAP 254 unit, equipped with a monochromatic low-pressure mercury arc, allowed irradiations at 254 nm.

The photo-oxidized samples were submitted to various chemical treatments that permit, by derivatization, identification of the different photoproducts by FTIR spectrophotometry.

- Macromolecular hydroperoxides formed in the photo-oxidized sample were titrated by using a method based on the oxidation of Fe²⁺ in solution.¹⁵
- Irradiated films were exposed to SF₄ and NH₃ gases at room temperature, respectively in an all-Teflon reactor and in a glass flow system that could be sealed off to allow the reaction to proceed. SF₄ and NH₃ were supplied by Fluka and Ucar, respectively.
- Carboxylic acids are known to react with SF₄ to give acyl fluorides (RCOF). The acyl fluorides are characterized by a distinct IR absorption band in the range 1810–1845 cm⁻¹;^{16,17} the frequency of the maximum of this band is related to the structure of the acid. The SF₄ reaction gives a total disappearance of hydroxyl absorption (alcohols, hydroperoxides). Many aldehydes and ketones are converted to gem-difluoro compounds; esters are unreactive under our experimental conditions.
- Acid, ester and formate groups are known to react with NH₃ to give respectively ammonium carboxylates, amides and formamide.¹⁸ The ammonium carboxylates are characterized by an IR absorption band in the range 1560–1580 cm⁻¹, amides by an IR absorption band in the range 1660–1680 cm⁻¹ and formamide by an IR absorption band at 1690 cm⁻¹.¹⁹

For vacuum photolysis and thermolysis treatments, polymer samples were introduced into Pyrex tubes ($\lambda > 300$ nm) or quartz tubes ($\lambda = 254$ nm) and sealed under vacuum (10⁻⁶ torr), obtained with a Mercury diffusion vacuum line.

UV spectra were recorded on a Perkin-Elmer model 554 instrument equipped with an integrating sphere. IR spectra were recorded on a Nicolet 510 FTIR spectrophotometer (nominal resolution of 4 cm^{-1} , summation of 30 scans). Measurements of photoproduct profiles in irradiated films were performed on a Nicolet 800 FTIR spectrophotometer coupled to a NicPlan microscope (nominal resolution of 8 cm^{-1} , summation of 128 scans).²⁰

Oxygen permeability was measured with a Lyssy GPM 200 apparatus. MS analysis of low-molecular-weight photoproducts trapped in irradiated films was performed by using a Balzers type QMG 421 (1–200 amu) quadrupole mass spectrometer system. Gas chromatography (GC)/MS analysis of photoproducts, extracted from photo-oxidized films by immersion in MeOH, were performed with a 5989 series mass-selective detector (Hewlett-Packard).

3 PHOTO-OXIDATION AT LONG WAVELENGTHS ($\lambda > 300\text{ nm}$)

3.1 Analysis of IR and UV spectra

Irradiation of thin PR films ($25\text{--}50\ \mu\text{m}$) under polychromatic light obtained from filtered medium-pressure mercury lamps ($\lambda > 300\text{ nm}$, 60°C) in the presence of air leads to noticeable variations in the IR and UV spectra of exposed films.

- In the region $1900\text{--}1500\text{ cm}^{-1}$ [Fig. 1(A)], photo-oxidation leads to the formation of a narrow absorption band with a maximum at 1739 cm^{-1} after 3 h exposure. As photo-oxidation proceeds, two distinct phases are observed in the development of the complex carbonyl band.
 - During the first 210 h of irradiation, the intensity of the carbonyl band increases and the maximum at 1739 cm^{-1} is shifted progressively to 1734 cm^{-1} . Two shoulders detected at 1680 cm^{-1} and 1657 cm^{-1} are attributed to the absorption of photoproducts respectively called P_{1680} and P_{1657} .
- After this period, the carbonyl absorbance reaches a limiting value and the maximum is shifted to 1725 cm^{-1} . Subtractions of successive IR spectra [for instance, 590 h minus 400 h, Fig. 1(B)] show that final photoproducts are characterized by an absorption band with a maximum at 1710 cm^{-1} , in the range of

vibration of aliphatic carboxylic acids. In parallel, photo-oxidation products with maxima at 1740 cm^{-1} and 1759 cm^{-1} are photolysed. Modification of ring substitutions induces the formation of an absorption maximum at 1593 cm^{-1} ; this observation is hampered on account of the decreasing initial absorption bands at 1608 cm^{-1} and 1582 cm^{-1} ($\nu_{\text{C-C ring}}$).

- In the region $3800\text{--}3100\text{ cm}^{-1}$, one can observe an important increase in the initial band at 3450 cm^{-1} . The maximum of this broad increase of absorption is shifted progressively from 3320 cm^{-1} to 3298 cm^{-1} [Fig. 1(C)]. The initial band at 3576 cm^{-1} , attributed to phenolic end-groups of PR,¹⁹ is observed to decrease.
- At the same time, a significant decrease in the intensity of the intrinsic absorption bands of the polymer occurs. For 139 h of irradiation, which corresponds to an increase in absorbance in the carbonyl range of close to 0.1, the relative absorbance decrease $[(\Delta OD/OD_0)\%]$ of monomer units of a $25\ \mu\text{m}$ thick film has

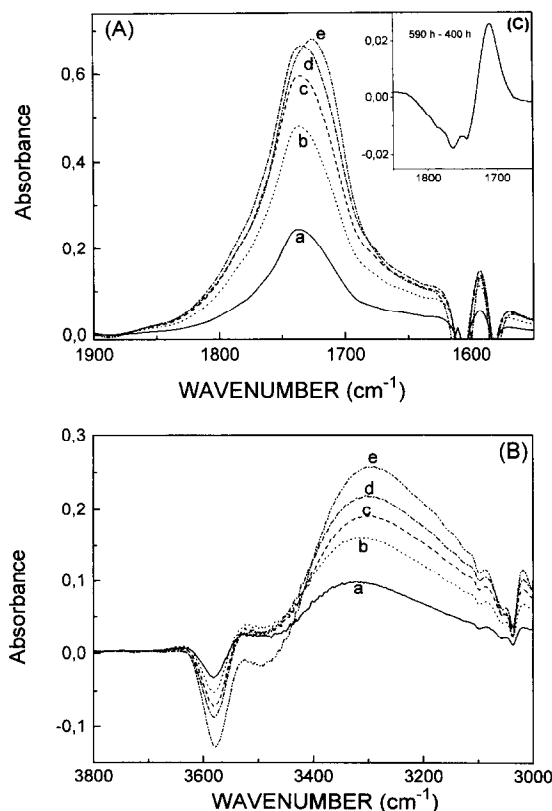


Fig. 1. Subtracted FTIR spectra between the non-irradiated and irradiated PR samples for various photo-oxidation times ($\lambda > 300\text{ nm}$, 60°C): (a) 47 h; (b) 94 h; (c) 140 h; (d) 211 h; (e) 590 h. (A) Carbonyl vibration region; (B) hydroxyl vibration region; (C) subtraction of the spectrum of the film photo-oxidized for 590 h from the spectrum of the film photo-oxidized for 400 h.

been computed and the following observations can be derived.

- Irradiation mainly involves disappearance of the ether band (decrease of 10% at 1042 cm^{-1}).
- $\text{CH}_3\text{-C}$ cleavage in the isopropylidene group also occurs to a large extent (9% at 1183 cm^{-1}). The rearrangement of CH_3 groups from isopropylidene structure to $\text{-CH}_2\text{-}$ groups has been observed previously throughout the photo-oxidation of bisphenol-A polycarbonate.¹⁴
- The diminution of the 1582 cm^{-1} band (quadrant stretching of the benzene ring, decrease of 7%), accompanied by the development of the band at 1593 cm^{-1} , may be related to benzene substitution. Claisen and photo-Fries rearrangements have been proposed in the literature⁶ to account for this modification.
- Hydrogen abstraction from -CH_3 , -CH_2 and aromatic rings occurs to a smaller extent (decrease of 3%). The decrease in -CH_2 content throughout photo-oxidation is postulated to be overlapped by the probable rearrangement of -CH_3 groups to -CH_2 groups.
- Only little information can be derived concerning the photochemical behaviour of the -CH(OH)- units. The IR vibration of the C-H group (2890 cm^{-1}) is masked by the more intense absorption bands of methylene and methyl groups; and the evolution of initial -OH groups is overlapped by the formation of hydroxylated photoproducts.
- The change in the UV spectra of PR films throughout irradiation (Fig. 2) shows a gradual

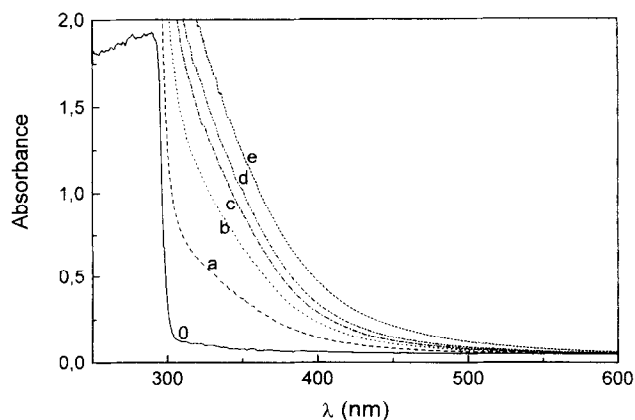


Fig. 2. Changes of the UV-VIS spectra of PR film photo-oxidized at $\lambda > 300\text{ nm}$ and 60°C for: (a) 47 h; (b) 94 h; (c) 140 h; (d) 211 h; (e) 590 h.

increase of light absorption from 270 nm to 500 nm without any maximum. This absorption accounts for the appearance of the yellow discoloration of the polymer films.

3.2 Photo-oxidation rate

A fast rate of oxidation is observed within the first 210 h of exposure. After this period, the kinetic curves corresponding to the formation of IR- and UV-absorbing photoproducts reach an invariant state [Fig. 3(A)]. A decrease in polymer content is observed throughout the exposure [Fig. 3(B)].

These two kinetic variations can be explained on the basis of photolysis of the oxidation products observed at 1740 cm^{-1} and 1759 cm^{-1} . Therefore, photoproduct concentration reaches a stationary value and the polymer is oxidized layer by layer. Analysis of the gas phase by mass spectrometry allowed us to identify acetic and formic acids among the volatile photoproducts. These results prompted us to assign the final oxidation band observed at 1710 cm^{-1} to the

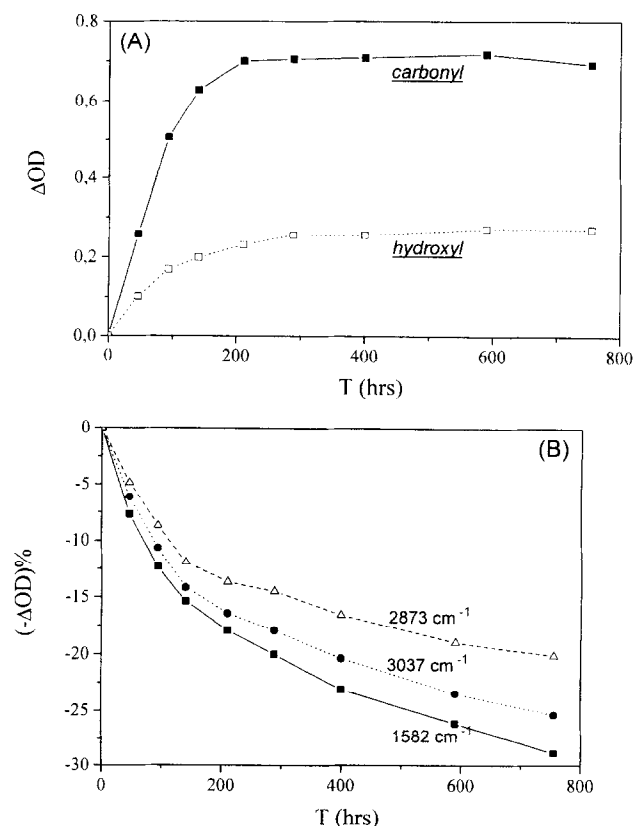


Fig. 3. (A) Increase of absorbance versus irradiation time of a PR film photo-oxidized at $\lambda > 300\text{ nm}$, 60°C for the IR absorptions in the carbonyl (■) and hydroxyl (□) ranges. (B) Variations of absorbance at 2873 cm^{-1} (△), at 3037 cm^{-1} (●) and at 1582 cm^{-1} (■) on photo-oxidation at $\lambda > 300\text{ nm}$, 60°C .

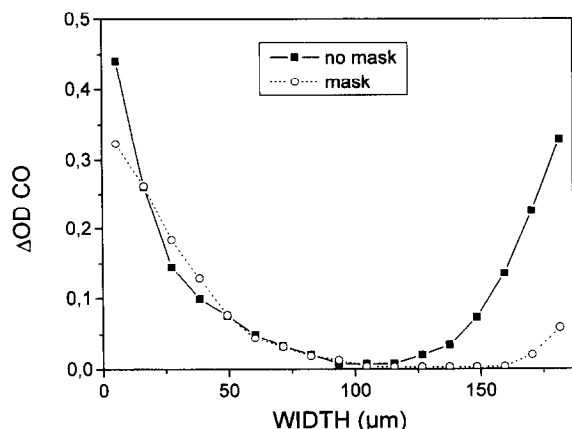


Fig. 4. Photo-oxidation profile measured by micro-FTIR of PR films (190 μm) irradiated for 145 h at $\lambda > 300$ nm, 60°C: (○) irradiation without a mask; (■) irradiation with a mask at the rear side.

dimer form of acetic and formic acids that are trapped in the matrix and that may diffuse out of the sample. The diffusion of low-molecular-weight products is responsible for the decrease in PR content previously observed in the FTIR spectra.

3.3 Determination of oxidation profiles

Two 190 μm thick samples were exposed for 145 h at $\lambda > 300$ nm, 60°C; the rear of one of the two samples was masked during irradiation. The oxidation profiles were determined by recording spectra every 11 μm . Optical density at 1735 cm^{-1} was measured and plotted (Fig. 4) as a function of the distance from the exposed face. It is observed from Fig. 4 that the photo-oxidation products are formed essentially on the external layers of the film. No oxidation photoproducts are observed in the core of the sample.

In order to understand the origin of this heterogeneous oxidation, the permeability of PR before and after exposure was determined. The data obtained are listed in Table 1 as well as the permeability of low-density polyethylene (PE), which is considered to be a relatively permeable polymer. The data suggest that the heterogeneous distribution of photoproducts has to be mainly attributed to limited oxygen diffusion: initially,

Table 1. Permeability ($\text{ml m}^2 24 \text{ h atm}$) of 100 μm polymer films

Polymer	Permeability (USI)
Low-density PE	1250–1750
Virgin PR	50
PR irradiated for 10 h at $\lambda > 300$ nm, 60°C	36
PR irradiated for 140 h at $\lambda = 254$ nm, 25°C	26

oxygen permeability is fairly low and it decreases greatly throughout irradiation.

The heterogeneity has also to be partly attributed to attenuation of the UV light intensity with distance to the exposed front layers, since it can be observed from the UV–visible spectra that photoproducts absorbing in this region are formed under exposure. Such species therefore decrease the penetration of long wavelengths ($\lambda > 300$ nm) into the irradiated films.

3.4 Identification of the photoproducts by derivatization reactions

3.4.1 Ammonia treatments

NH_3 treatments were carried out on 100 μm PR films that had been photo-oxidized at $\lambda > 300$ nm, 60°C for different periods of time: 3 h [Fig. 5(A)], 24 h, 260 h and 505 h [Fig. 5(B)].

Reaction of 3 h photo-oxidized PR films with NH_3 (18 h) leads to a decrease in the band at 1739 cm^{-1} and to the concomitant formation of a

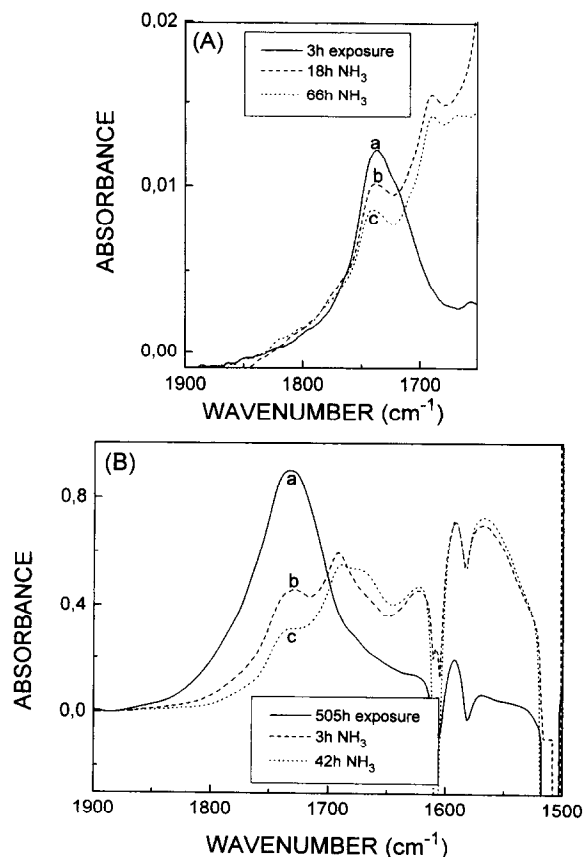


Fig. 5. (A) Changes of the IR spectra (subtraction of the initial spectrum) of a PR film photo-oxidized for 3 h at $\lambda > 300$ nm, 60°C (a) and then treated by NH_3 for 18 h (b) and 66 h (c). (B) Changes of the IR spectra (subtraction of the initial spectrum) of a PR film photo-oxidized for 505 h at $\lambda > 300$ nm, 60°C (a) and then treated by NH_3 for 3 h (b) and 42 h (c).

band at 1690 cm^{-1} assigned to the stretching vibration of a formamide (NH_2COH). Comparison was made with phenyl formate (1740 cm^{-1}) introduced into a PR polymer sample and then treated with NH_3 : reaction with NH_3 is observed to lead to the decrease of the carbonyl absorption at 1740 cm^{-1} and to the formation of the formamide band at 1690 cm^{-1} . The band that develops at 1739 cm^{-1} in photo-oxidized PR films has to be unambiguously attributed to phenyl formate end-groups on the basis of IR frequency and basic treatment.

For longer duration of NH_3 treatment (66 h), the formamide absorption at 1690 cm^{-1} is accompanied by the appearance of a shoulder at 1669 cm^{-1} . In addition, for longer exposure time ($>24\text{ h}$), the development of an absorption maximum at 1570 cm^{-1} is also observed. The band at 1669 cm^{-1} is assigned to the vibration of amide groups ($\text{NH}_2\text{CO}_2\text{R}$, amide I band) which result from the conversion of esters. The absorption at 1570 cm^{-1} ($\text{RCOO}^-\text{NH}_4^+$) corresponds to the carboxylate ion band obtained by neutralization of the carboxylic acid structure.

The results of NH_3 treatment are in good agreement with the stoichiometry of photo-oxidation: when the irradiation time of the film increases, the intensity of the carboxylate ion band was also observed to increase.

The participation of carboxylic acids and esters in the whole carbonyl absorption is very weak; phenyl formate end-groups have to be considered as the main photoproduct formed in the irradiated matrix.

3.4.2 SF_4 treatment

SF_4 has the undesirable effect of reacting with initial hydroxyl groups and with OH groups of α -hydroxylated photoproducts, and therefore leads to the development of parasite bands.

Treatment by SF_4 (Fig. 6) induces a weak decrease in the intensity of bands at 1713 cm^{-1} , 1739 cm^{-1} and 1755 cm^{-1} and the formation of three absorption bands at 1840 cm^{-1} , 1809 cm^{-1} and 1897 cm^{-1} .

The absorption maxima at 1713 cm^{-1} (dimer), 1755 cm^{-1} (monomer) and 1840 cm^{-1} have to be attributed respectively to the vibrations of saturated carboxylic acid and the derived acyl fluoride.

The band at 1897 cm^{-1} can be attributed to the acyl fluoride derived from oxalic acid [$\text{HO}-\text{C}(\text{O})-\text{C}(\text{O})\text{OH}$]. Such an assertion is based on

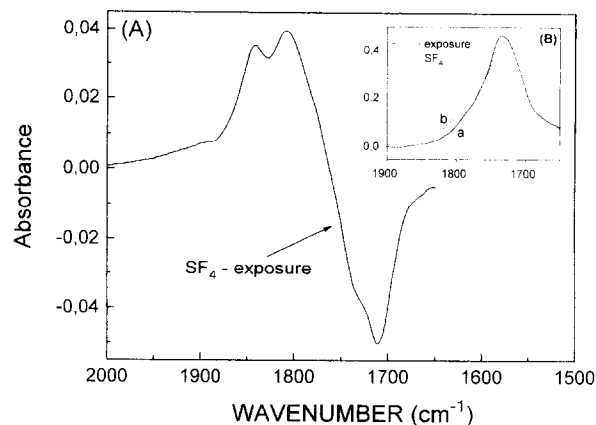


Fig. 6. (A) Changes of the IR spectra (subtraction: after treatment minus before treatment) of a PR film photo-oxidized for 92 h at $\lambda > 300\text{ nm}$, 60°C and then treated by SF_4 for 69 h. (B) Subtraction of the initial spectrum: (a) before treatment minus initial spectrum; (b) after treatment minus initial spectrum.

SF_4 treatment of molecular oxalic acid (1727 cm^{-1}) introduced into virgin PR film: it leads to the formation of derived acyl fluoride at 1897 cm^{-1} . In the same way, the bands at 1739 cm^{-1} and at 1809 cm^{-1} (as well as part of the band at 1840 cm^{-1}) have to be attributed respectively to the vibrations of tartronic acid [$\text{HO}-\text{CO}-\text{CH}(\text{OH})-\text{CO}-\text{OH}$] and the derived acyl fluoride.

Part of the band at 1809 cm^{-1} has to be also attributed to the acyl fluoride of benzoic acid (1697 cm^{-1}), which has been identified by GC/MS analysis of the methanolic extract.

It is still observed from Fig. 6 that the participation of carboxylic acids in the whole carbonyl absorption is very weak.

3.4.3 Methanol treatment. GC/MS analysis of the extract

Immersion of photo-oxidized PR films in methanol leads to a decrease in the absorbance of photo-oxidation products after 24 h in the solvent, the decrease of absorbance being observed to be more important in the IR range than in the UV-visible range. In the difference IR spectra (methanol treatment minus photo-oxidation), Fig. 7, the decrease of two absorption bands with maxima at 1727 cm^{-1} and 1739 cm^{-1} is observed. The absorption bands that decrease correspond to low-molecular-weight carboxylic acids that have been extracted by the solvent; i.e. oxalic acid and tartronic acid, respectively. Most of the decrease at 1739 cm^{-1} is attributed to alcoholysis reaction of phenyl formate end-groups by methanol.

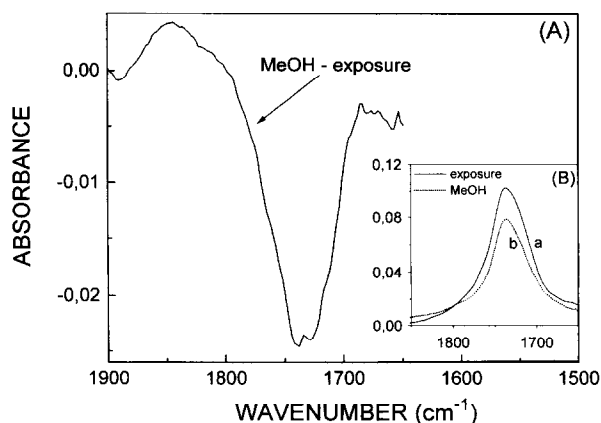


Fig. 7. (A) Changes of the IR spectra (subtraction: after immersion minus before immersion) of a PR film photo-oxidized for 25 h at $\lambda > 300$ nm, 60°C and then immersed in MeOH for 94 h. (B) Subtraction of the initial spectrum: (a) before immersion minus initial spectrum; (b) after immersion minus initial spectrum.

A GC/MS analysis of the methanol used to extract the oxidation photoproducts from PR films revealed the presence of two low-molecular-weight photoproducts identified as benzoic acid and acetic acid; the concentration of these two photoproducts is fairly low.

3.5 Identification of the photoproducts by vacuum physical treatments

Vacuum physical treatments of pre-photo-oxidized films were carried out to identify photo-unstable and thermo-unstable species (such as hydroperoxides and ketones) as well as low-molecular-weight photoproducts that may migrate out of the matrix.

3.5.1 Thermolysis at 100°C of photo-oxidized samples

Thermolysis at 100°C *in vacuo* of films pre-photo-oxidized for 261 h at $\lambda > 300$ nm induces a decrease in the intensity of the maxima at 1710 cm^{-1} , 1744 cm^{-1} and 1759 cm^{-1} ; an absorption band is observed to develop at 1726 cm^{-1} (Fig. 8, curve a).

- The decrease in the band at 1710 cm^{-1} indicates a loss of low-molecular-weight carboxylic acids, identified as acetic and formic acid by means of MS analysis of the gas phase.
- Comparison with data from the literature permits us to attribute the maxima at 1759 cm^{-1} and 1744 cm^{-1} to phenyl alkylate ($-\text{Ph}-\text{O}-\text{CO}-\text{R}$) and to aliphatic ester ($\text{R}_1-\text{O}-\text{CO}-\text{R}_2$), respectively. Such an assignment is in good accordance with NH_3 derivatization reactions.

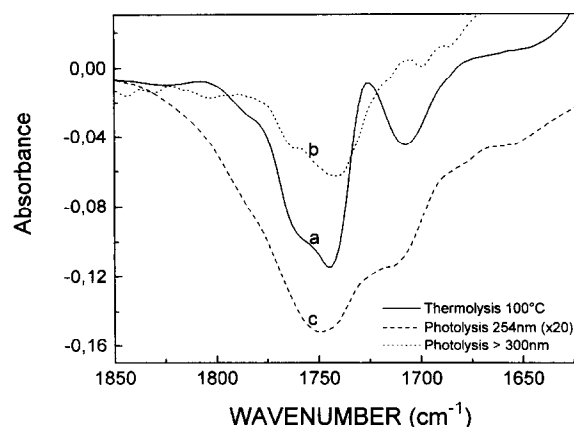


Fig. 8. Vacuum treatments of PR film pre-photo-oxidized at $\lambda > 300$ nm, 60°C for 261 h. Subtractions: after vacuum treatment minus before vacuum treatment. (a) Thermolysis in vacuum at 100°C for 183 h minus photo-oxidation at $\lambda > 300$ nm, 60°C for 261 h; (b) photolysis in vacuum at 254 nm for 1 h minus photo-oxidation at $\lambda > 300$ nm, 60°C for 21 h (absorbance is multiplied by 20); (c) photolysis in vacuum at $\lambda > 300$ nm, 60°C for 186 h minus photo-oxidation at $\lambda > 300$ nm, 60°C for 261 h.

This decrease of intensity at 1759 cm^{-1} and 1744 cm^{-1} can be correlated to the increase of the absorption at 1726 cm^{-1} which is in the range of α -unsaturated ester.¹⁹ Phenyl alkylate (1759 cm^{-1}) and aliphatic ester (1744 cm^{-1}) are postulated to be α -hydroxylated species: elimination of H_2O would occur under thermolysis in vacuum at 100°C ; according to Lin *et al.*,⁶ such a reaction could be followed by Claisen condensation.

3.5.2 Photolysis at $\lambda > 300$ nm of pre-photo-oxidized films

Photolysis in the absence of oxygen at $\lambda > 300$ nm of PR films photo-oxidized for 261 h at $\lambda > 300$ nm induces a decrease of the absorption bands with a large maximum around 1745 cm^{-1} , accompanied by a shoulder at 1715 cm^{-1} (Fig. 8, curve c). The decrease of absorbance is observed to be more important in photolysis at 60°C than in thermolysis at 100°C .

- The decrease at 1715 cm^{-1} is assigned to the loss of low-molecular-weight carboxylic acids (acetic and formic acids) which migrate out of the matrix.
- The broad band with a maximum around 1745 cm^{-1} is assigned to the photo-thermal instability of three photoproducts:
 - The aromatic and aliphatic esters (1759 cm^{-1} and 1744 cm^{-1}), which were shown to be thermo-unstable (dehydration).

- Part of the instability of the broad band at 1745 cm^{-1} is due to photolysis of two aromatic species: phenyl formate end-groups (1739 cm^{-1}) and phenyl alkylate (1759 cm^{-1}). The photo-Fries rearrangement of the phenyl alkylate may occur leading to the formation of *ortho*-hydroxyphenone structure.¹⁴ The rate of photolysis is observed to be fairly low.
- The photo-instability of P_{1657} and of P_{1680} is also observed.

3.5.3 Photolysis at 254 nm of pre-photo-oxidized films

A PR film photo-oxidized for 21 h at $\lambda > 300\text{ nm}$ was submitted to a further irradiation at 254 nm in the absence of oxygen at 25°C (Fig. 8, curve b). Photolysis at 254 nm is observed to induce a weak decrease of two bands assigned to aromatic structures: phenyl formate (1739 cm^{-1}) and phenyl alkylate (1759 cm^{-1}). The photo-instability of P_{1657} and P_{1680} also occurs.

When pre-exposure at $\lambda > 300\text{ nm}$ was carried out for 357 h, irradiation at 254 nm was observed to provoke elimination of the superficial oxidized layer (it will be seen later that irradiation at 254 nm is intrinsically a surface phenomenon).

4 PHOTO-OXIDATION AT SHORT WAVELENGTH ($\lambda = 254\text{ NM}$)

PR has its main band in the medium UV range ($\lambda = 276\text{ nm}$), and its long-wavelength tail continues until 400 nm. Thus, while the absorption of the polychromatic light ($\lambda > 300\text{ nm}$) by the polymer is fairly low, the short-wavelength radiation ($\lambda = 254\text{ nm}$) is completely absorbed by the aromatic chromophoric groups.

It appears that there are many similarities in the nature of the photoproducts formed at long wavelengths ($\lambda > 300\text{ nm}$) and at short wavelength ($\lambda = 254\text{ nm}$). Thus only the differences will be emphasized.

Irradiation of PR films at 254 nm in the presence of air induces a decrease of the absorption bands of the polymer and leads to the formation of photoproducts absorbing in the carbonyl, hydroxyl and UV ranges.

- Photoproducts formed in the UV—visible and hydroxyl ranges [Fig. 9(B)] appear to be analogous to those observed at $\lambda > 300\text{ nm}$.
- In the carbonyl range [Fig. 9(A)], the band that initially develops at 1734 cm^{-1} is observed to

shift to 1725 cm^{-1} when exposure time increases: the formation of carboxylic acid groups (1710 cm^{-1}) was observed to explain such an occurrence.

The two shoulders at 1680 cm^{-1} and at 1657 cm^{-1} , previously attributed to the absorption of P_{1680} and P_{1657} , are more easily observed than under exposure at $\lambda > 300\text{ nm}$.

- After 70 h of irradiation, which corresponds to an increase in absorbance in the carbonyl range of close to 0.11, the percentage decrease in the intrinsic absorption bands of the polymer has been computed: the consumption of all the initial bands of the polymer ($-\text{CH}_3$, $-\text{CH}_2$, ether, rings) is roughly 10%.
- As observed at $\lambda > 300\text{ nm}$, the kinetic curves show that the photoproduct concentrations reach a photostationary value whilst the decrease of the polymer absorption bands is observed throughout the exposure; it can be anticipated that the loss by migration of the low-molecular-weight acids accounts for such experimental results.

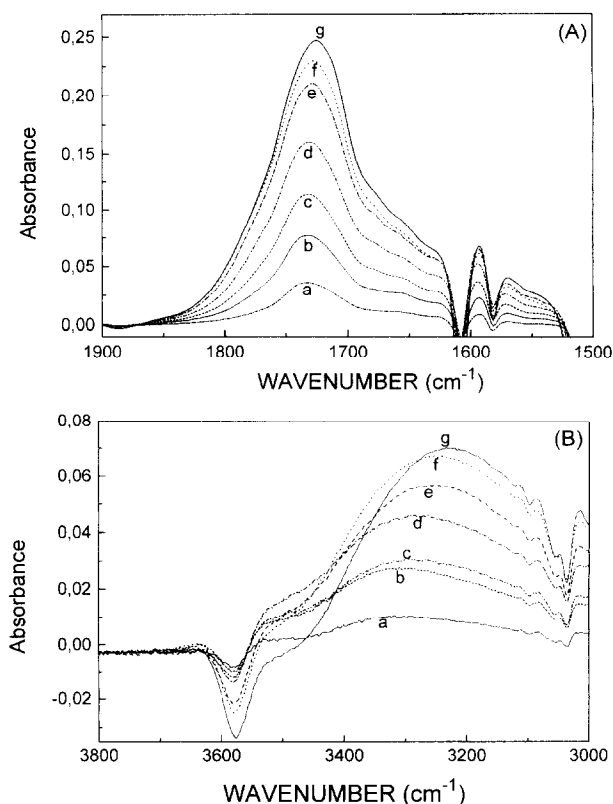


Fig. 9. Subtracted FTIR spectra between the non-irradiated and the irradiated PR samples for various photo-oxidation times ($\lambda = 254\text{ nm}$, 25°C): (a) 24 h; (b) 46 h; (c) 70 h; (d) 115 h; (e) 233 h; (f) 327 h; (g) 661 h.

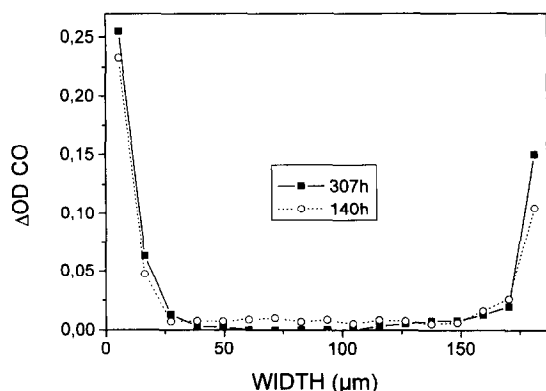


Fig. 10. Photo-oxidation profile measured by micro-FTIR of PR films (190 μm) irradiated for 140 h (○) and 307 h (■) at $\lambda = 254$ nm, 25°C.

- Concentration profiles were determined for PR films (thickness 190 μm) irradiated at 254 nm for 140 h and 307 h. Microspectrometric measurements reported in Fig. 10 reveal that the oxidation photoproducts appear only in the first 25 μm and that most of the photo-oxidation occurs in the first 11 μm . Photo-oxidation at 254 nm appears to be a more superficial reaction than that at $\lambda > 300$ nm. As opposed to long-wavelength exposure ($\lambda > 300$ nm), irradiation at 254 nm is intrinsically a surface reaction: 90% of the incident light is absorbed in the first 3 μm thick superficial layer.

4.1 Identification of the photoproducts by derivatization reactions

4.1.1 Hydroperoxide titrations

The concentration of hydroperoxides remains unimportant throughout exposure (1 mmol kg^{-1}); hydroperoxides are photo-unstable under irradiation at 254 nm and at $\lambda > 300$ nm.

4.1.2 Ammonia treatments

One of the main differences between short- and long-wavelength exposure lies in the reactivity of photo-oxidized films with NH_3 . Reaction of photo-oxidized PR films with NH_3 leads to the decrease of the carbonyl band (Fig. 11) and to the development of three absorption maxima

- at 1669 cm^{-1} (amide I) and at 1625 cm^{-1} (amide II): absorption bands of amide groups which result from the reaction of esters with NH_3 .
- at 1570 cm^{-1} : carboxylate absorption which results from the neutralization of acid groups with NH_3 .

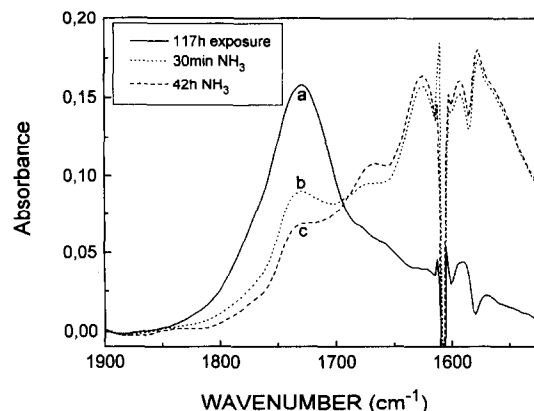


Fig. 11. Changes of the IR spectra (subtraction of the initial spectrum) of a PR film photo-oxidized for 117 h (a) at $\lambda = 254$ nm, 25°C and then treated by NH_3 for 30 min (b) and 42 h (c).

When the oxidized film is exposed for longer than 24 h in the SEPAP 254 unit, there is no evidence for the presence of formate since no derivative band is observed to develop at 1690 cm^{-1} . At a fairly low degree of conversion, reaction of the photo-oxidized film with NH_3 leads to the appearance of a weak shoulder at 1690 cm^{-1} which could be attributed to formamide ($\text{NH}_3 + \text{phenyl formate}$).

Vacuum photolysis at 254 nm and at $\lambda > 300$ nm of films pre-photo-oxidized at $\lambda > 300$ nm has shown that the photo-stability of phenyl formate is less good at short wavelength than at long wavelengths. It can therefore be concluded that the main difference between short- and long-wavelength exposure lies in the contribution of phenyl formate end-groups to the carbonyl absorption: phenyl formate end-groups are the main photoproducts that accumulate under irradiation at $\lambda > 300$ nm whilst their concentration is insignificant at $\lambda = 254$ nm.

4.1.3 SF_4 treatments

Reaction of photo-oxidized PR films with SF_4 leads to changes similar to those reported above for samples photo-oxidized at $\lambda > 300$ nm.

- Saturated carboxylic acids are converted into acyl fluorides which absorb at 1840 cm^{-1} .
- Oxalic acid is formed, the derivative of which is observed at 1897 cm^{-1} .

Two differences between the two exposures are observed.

- The derivative band that is observed at 1809 cm^{-1} is assigned to the acyl fluoride of benzoic acid (1697 cm^{-1}), as identified by GC/MS

analysis of the methanolic extract. No tartronic acid (1734 cm^{-1}) is evidenced by SF_4 treatment.

- The contribution of the carboxylic acid at 1710 cm^{-1} is much higher for irradiation at short wavelength.

4.1.4 Methanolic treatment

Immersion of photo-oxidized PR films in CH_3OH leads to an important decrease in the absorbance of photo-oxidation products that absorb in the carbonyl and UV ranges. GC/MS analysis of the solvent confirms the identification of the photo-products deduced from the derivatization reactions: acetic and benzoic acid.

4.2 Identification of the photoproducts by vacuum physical treatments

4.2.1 Thermolysis at 100°C

Thermolysis of photo-oxidized films at 100°C under vacuum leads to a decrease of the absorption bands with maxima at 1710 cm^{-1} , 1748 cm^{-1} (Fig. 12, curve a) and 3345 cm^{-1} .

- The band at 1710 cm^{-1} (dimer acid), part of the band at 1748 cm^{-1} (monomer acid at 1755 cm^{-1}) and the absorption at 3345 cm^{-1} are assigned to low-molecular-weight carboxylic acids trapped in the matrix. As observed with SF_4 treatment, the contribution of carboxylic acid to the carbonyl absorption is much higher for irradiation at 254 nm .

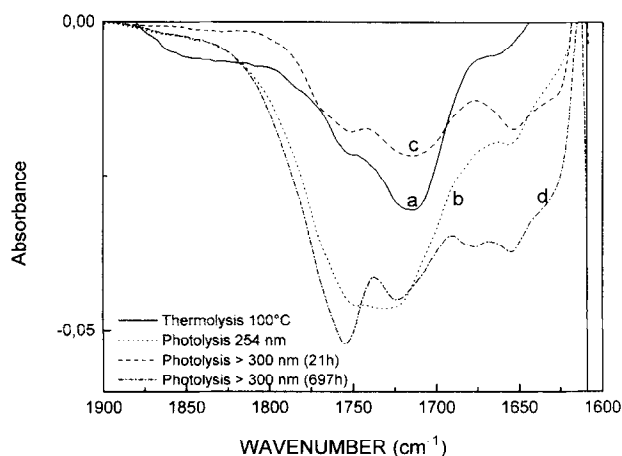


Fig. 12. Vacuum treatments of PR film pre-photo-oxidized at $\lambda = 254\text{ nm}$, 25°C for 117 h. Subtractions: after vacuum treatment minus before vacuum treatment. (a) Thermolysis in vacuum at 100°C for 173 h minus photo-oxidation at 254 nm for 117 h; (b) photolysis in vacuum at 254 nm for 181 h minus photo-oxidation at 254 nm for 117 h; (c) and (d) photolysis in vacuum at $\lambda > 300\text{ nm}$, 60°C for 21 h (c) and 697 h (d) minus photo-oxidation at 254 nm for 117 h.

- Dehydration of α -hydroxylated alkylate (identified by NH_3 treatment) accounts also for the decrease of the absorption at 1748 cm^{-1} and at 3345 cm^{-1} .

On long exposure, the band that is observed to develop at 1675 cm^{-1} is assigned to unsaturated species resulting from a dehydration reaction of the α -hydroxylated photoproducts.

4.2.2 Photolysis at 254 nm

A marked decrease in the absorption of photo-products is observed in IR spectra throughout photolysis at 254 nm , in the absence of oxygen, of films pre-photo-oxidized at 254 nm . The subtractions of spectra (after photolysis minus before photolysis) show that the decrease of absorption is unstructured (Fig. 12, curve b).

These results confirm that some of the photoproducts formed on photo-oxidation of PR are low-molecular-weight compounds. This behaviour can be also attributed to the photolysis of oxidation photoproducts formed along with important chain scissions, which are then transformed into low-molecular-weight products. The elimination of the superficial layer from the irradiated film that occurs under exposure accounts for the stationary values reached for photoproduct concentrations when the PR films are photo-oxidized at 254 nm .

4.2.3 Photolysis at $\lambda > 300\text{ nm}$

Irradiation of photo-oxidized film sealed under vacuum was performed at $\lambda > 300\text{ nm}$, 60°C . Two phases are involved in the vacuum irradiation (Fig. 12, curve c and d).

- Under short exposure, the photo-instability of three maxima is revealed by the subtraction of spectra (Fig. 12, curve c):
 - at 1710 cm^{-1} : low-molecular-weight carboxylic acid (dimer),
 - at 1755 cm^{-1} : carboxylic acid (monomer) and phenyl alkylate which undergoes photo-Fries rearrangement. This leads to the formation of *o*-hydroxyphenone, which easily photolysed in the matrix, and
 - at 1657 cm^{-1} : elimination of P_{1657} .
- Under long exposure, the instability of two additional photoproducts is revealed (Fig. 12, curve d): P_{1680} at 1680 cm^{-1} and saturated ketone at 1725 cm^{-1} .

As previously emphasized, P_{1657} and P_{1680} have to be considered as photo-unstable structures; their IR absorption is in the range of conjugated ketonic structures. Derivatization treatments provided insufficient data on the behaviour of these two photoproducts: therefore, the chemical structures of P_{1657} and P_{1680} cannot be established definitively.

5 VACUUM PHOTOLYSIS

As observed from the initial UV-visible spectrum, the intrinsic chromophoric units in virgin PR film (i.e. the phenyl ether group) can absorb the polychromatic incident light up to the near-UV range; it is also emphasized that the critical domain for the photolysis of PR corresponds to the range 300–350 nm, owing to the absorption of the polymer.

Irradiation of PR films *in vacuo* at $\lambda > 300$ nm, 60°C leads to slight changes in the IR and UV spectra.

- The changes occurring in the FTIR spectra in the carbonyl and hydroxyl domains are observed to be weak and to parallel the consumption of all the initial bands of the polymer (mainly the C–O–C band at 1042 cm^{-1} and the C–CH₃ band at 1182 cm^{-1}):
 - in the carbonyl range, the formation of a band at 1737 cm^{-1} occurs with a shoulder around 1720 cm^{-1} [Fig. 13(A)];
- in the hydroxyl region [Fig. 13(B)], a broad band develops with a maximum around 3320 cm^{-1} and the initial band of phenolic end-groups of PR at 3576 cm^{-1} is observed to decrease.
- On the basis of phototransformation rates in the presence of oxygen and in vacuum (Fig. 14), the occurrence of direct photolytic processes can be considered to be negligible compared with photo-oxidation processes.
- In the UV-visible range, it is observed that photolysis results in a slight increase in light absorption from 300 to 450 nm without any maximum.
- MS analysis of the gas phase formed during vacuum exposure permits the unambiguous identification of methane and water.

Irradiation in vacuum of PR films at $\lambda = 254$ nm was observed to be roughly similar to that

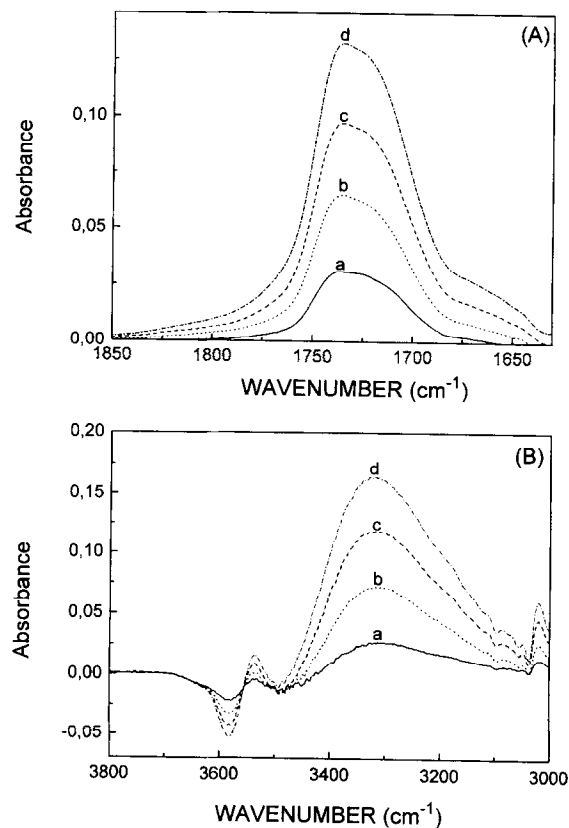


Fig. 13. Subtracted FTIR spectra between the non-irradiated and the irradiated PR samples for various vacuum photolysis times ($\lambda > 300$ nm, 60°C): (a) 286 h; (b) 630 h; (c) 980 h; (d) 1296 h. (A) Carbonyl vibration region; (B) hydroxyl vibration region.

reported above for vacuum photolysis at $\lambda > 300$ nm, 60°C. The IR and UV spectral changes are, as under long-wavelength irradiation, of small importance and account for the formation of analogous hydroxylated and carbonylated species as well as for the yellow discoloration of the polymer.

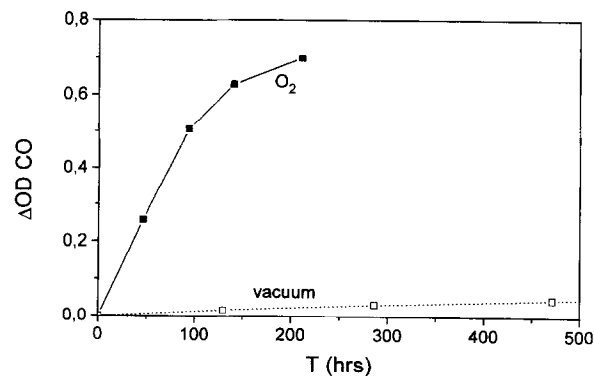


Fig. 14. Increase of absorbance versus irradiation time of a PR film irradiated at $\lambda > 300$ nm, 60°C for IR absorptions in the carbonyl range. (■) Irradiation in the presence of oxygen; (□) irradiation under vacuum.

Table 2. Characteristic absorptions of the photo-oxidation products and their identification methods

Photoproduct	IR frequency (cm ⁻¹)	Derivatization reaction	Physical treatment
ROOH		chemical titration	
Phenyl formate end-group*	1739	NH ₃ , 1690 cm ⁻¹ MeOH, solvolysis	photolysis at $\lambda > 300$ nm and $\lambda = 254$ nm
Phenyl alkylate	1759	NH ₃ , 1670 cm ⁻¹	photolysis, thermolysis
Saturated ester	1744	NH ₃ , 1670 cm ⁻¹	thermolysis
Acetic acid	1710 (dimer) 1755 (monomer)	SF ₄ , 1840 cm ⁻¹ NH ₃ , 1570 cm ⁻¹ MeOH, GC/MS	thermolysis (MS detection)
Formic acid	1710 (dimer) 1755 (monomer)	SF ₄ , 1840 cm ⁻¹ NH ₃ , 1570 cm ⁻¹	thermolysis (MS detection)
Oxalic acid	1727	SF ₄ , 1897 cm ⁻¹ MeOH	
Tartronic acid	1734	SF ₄ , 1809 cm ⁻¹	
Benzoic acid	1697	SF ₄ , 1809 cm ⁻¹ MeOH, GC/MS	
Aliphatic ketone† CH ₄ and H ₂ O‡	1725		photolysis at $\lambda > 300$ nm MS detection

*Photo-oxidation at $\lambda > 300$ nm. †Photo-oxidation at 254 nm. ‡Vacuum photolysis.

6 CONCLUSION

Table 2 lists the different photoproducts identified by analysis of the photo-oxidized samples.

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