

Polystyrene Photooxidation. 1. Identification of the IR-Absorbing Photoproducts Formed at Short and Long Wavelengths

Bénédicte Mailhot and Jean-Luc Gardette*

Laboratoire de Photochimie, URA CNRS 433, Université Blaise Pascal (Clermont-Ferrand), F-63177 Aubière Cedex, France

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ABSTRACT: Polystyrene films were exposed to radiation of long wavelength ($\lambda \geq 300$ nm) and short wavelength ($\lambda = 253.7$ nm) under atmospheric oxygen. Changes in the FTIR spectra of the photooxidized samples were followed, along with several postirradiation treatments including chemical derivatization reactions and HPLC analysis of the low molecular weight fragments that were obtained after extraction by methanol. The absorption maxima which were found in the carbonyl and hydroxyl regions of the infrared were assigned, and the corresponding photoproducts were identified.

Introduction

The reactions that are involved in the photooxidation of polystyrene (PS) have been extensively described in the scientific literature since the early work of Grassie.¹ It is however, surprising that many steps of the mechanisms remain unknown despite agreement on the main consequences of photooxidation, whose manifestations are an evolution of the chemical structure due to the formation of oxidized groups, the development of a discoloration, and the loss of the physical properties.^{2,3}

The photooxidation of polystyrene has been described essentially for irradiation at short wavelength ($\lambda = 253.7$ nm) that is absorbed by the styrene chromophoric groups. Different initiation steps have been proposed in the literature.⁴⁻⁸

Long-wavelength photooxidation has not received as much attention. Long-wavelength radiation ($\lambda \geq 300$ nm) is not absorbed by polystyrene. The initiation of photooxidation is generally accepted to result from light absorption by chromophoric impurities^{9,10} or by a charge-transfer complex.⁷

As pointed out above, the mechanism of photooxidation at short and long wavelengths cannot be considered as definitely established, even for short-wavelength photooxidation. A number of different photoproducts are formed, and a wide variety of mechanisms can be proposed. Moreover, no detailed study on the relationship between photooxidation at short wavelengths ($\lambda = 254$ nm) (wavelengths absorbed by the chromophoric group of PS) and photooxidation at long wavelengths ($\lambda \geq 300$ nm) (wavelengths leading to a photoinduced oxidation) has been published.

The formation of hydroperoxides as primary photoproducts is well established. Several types of secondary reactions are reported that involve direct photolysis, decomposition by energy transfer, and intramolecular decomposition and lead to the formation of carbonyl and hydroxyl compounds.^{4,11-14} Numerous structures have been proposed on the basis of IR and UV-visible analysis.¹⁵⁻¹⁷

Aromatic ketones formed by decomposition of tertiary hydroperoxides have been observed.¹⁸ Aliphatic ketones have also been reported;¹² they would be formed by oxidation of the secondary carbon atom on the polymeric backbone. Peroxyesters resulting from the formation of the aliphatic ketones have been detected in the IR spectrum of photooxidized polystyrene. Oxidation of the

aromatic ring has also been postulated, leading to the formation of muconaldehyde type structures.^{4,7,19} However, the main evidence for the formation of these products are the positions of the IR absorption maxima in the C=O domain.

Volatile products have been detected and identified:¹² water and carbon dioxide (which would result from a quantitative CO₂ loss by peroxyesters obtained by oxidation of the secondary hydroperoxides formed on the backbone). Benzaldehyde and acetophenone have also been identified, and they would result from Norrish type I and type II photolysis of the aromatic ketone.

The results on polystyrene photooxidation reported in this paper are part of a larger topic dealing with the photooxidation of physical blends based on styrene-acrylonitrile copolymers. Investigation of the behavior of these polymers requires a better knowledge of the mechanism of the photooxidation of polystyrene than given in the literature to date. The evolution of the analytical techniques now permits a better identification of the photoproducts.

The purpose of the present paper is to identify the oxidation photoproducts by means of FTIR spectroscopy coupled with derivatization reactions and physical treatments. In part 2 of the paper, a general mechanism of photooxidation will be proposed with a discussion on the connections between irradiation conditions (wavelength, temperature) and the photoproduct formation.

Experimental Section

Commercial polystyrene powder (Gedex) was supplied in 1984 by CdF Chimie. The powder contained no additive (e.g., antioxidant, lubricant, or plasticizer). It was pressed into thin films (100–200 μ m). The films were stored in the dark at 8 °C until needed. Before irradiation, the films were Soxhleted with methanol for 85 h and carefully dried in a vacuum oven at 70 °C for 72 h. Irradiations were carried out in a SEPAP 12-24 for long-wavelength irradiations ($\lambda \geq 300$ nm) at a temperature of 60 °C. The short-wavelength irradiations ($\lambda = 253.7$ nm) were carried out in a SEPAP 253.7 unit at a temperature of 30 °C. These units have been described in several papers (see, for example, refs 20 and 21).

Fourier transform IR (FTIR) spectra were recorded with either a Nicolet 20SX or a Nicolet 800 spectrometer, both equipped with a TGS detector. Spectra were obtained using 64 scan summations at a nominal resolution of 2 cm⁻¹.

Photooxidized films were exposed to reactive gas at room temperature in a simple flow system that could be sealed off to allow the reaction to proceed. SF₄ treatment was carried out in an

all-Teflon system because SF_4 attacks glass. The gases used included SF_4 and NH_3 (supplied respectively by Fluka and UCAR).

For comparison purposes, model compounds were studied. These compounds were introduced by permeation into polystyrene films and then reacted with the gases. IR spectra were recorded before and after the derivatization reactions. All model compounds (acetic acid, hexanoic acid, 2-phenylbutyric acid, benzoic acid, δ -valerolactone) were used as supplied.

For thermolysis experiments, photooxidized samples were heated in a vacuum oven.

For photolysis experiments, polymer samples were degassed and sealed in Pyrex tubes (for long-wavelength irradiation) or quartz tubes (short-wavelength irradiation) under vacuum (10^{-6} Torr, obtained using a mercury diffusion vacuum line).

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 ratios varying from 9:1 to 6:4. The outflow was 1 mL/min.

Experimental Results and Discussion

1. Photooxidation at "Long Wavelength" ($\lambda \geq 300$ nm). Irradiation of polystyrene films (thickness $89 \mu\text{m}$) under the standard conditions of the SEPAP 12-24 unit (temperature 60°C) in the presence of air leads to noticeable evolutions of their IR spectra. The main evolutions occur in the IR domains that are characteristic of the carbonylated and hydroxylated compounds and they correspond to an increase of absorbance over a broad range. Figure 1 shows these evolutions in the 1900 – 1500 - and 3800 – 3100 - cm^{-1} regions, which correspond respectively to the domains where the $\text{C}=\text{O}$ and OH stretching vibrations.

Subtraction of the initial spectrum before irradiation from the spectra recorded after several irradiation times allows the observation of the global shape of the broad carbonyl and hydroxyl absorption bands that are formed (Figure 2).

Several maxima or shoulders are observed in the carbonyl band: 1690 , 1698 , 1732 , and 1785 cm^{-1} . These bands result from the convolution of several bands whose maxima will be determined later by derivatization reactions. A weak band is formed at 1515 cm^{-1} , and an absorption band with a maximum around 1605 cm^{-1} can be noticed even if the observation is hampered on account of the important initial absorption band of polystyrene at 1600 cm^{-1} that interferes in the subtraction of the spectra.

The broad hydroxyl band that is formed is centered around 3450 cm^{-1} . A narrow band with a high intensity is observed in the same region, with an absorption maxima at 3540 cm^{-1} and a weak band at 3250 cm^{-1} .

Identification of the Photoproducts by Derivatization Reactions. Several derivatization reactions have been used for identifying the oxidation photoproducts which are observed by IR analysis. These reactions include treatment by gases (sulfur tetrafluoride, ammonia).

Sulfur Tetrafluoride Reactions. Many aldehydes and ketones are converted to *gem*-difluoro compounds with sulfur tetrafluoride (SF_4). Esters also give trifluorides but under more vigorous conditions which are far off the experimental method.²² Carboxylic acids also react with SF_4 to give 1,1,1-trifluorides.²² The first product of this reaction is an acyl fluoride that can be isolated:



The reactions with carboxylic acids to give acyl fluorides and alcohols/hydroperoxides to give alkyl fluorides are the most likely to occur.

The SF_4 reaction has indeed been used to measure quantitatively the carboxylic acid groups formed in

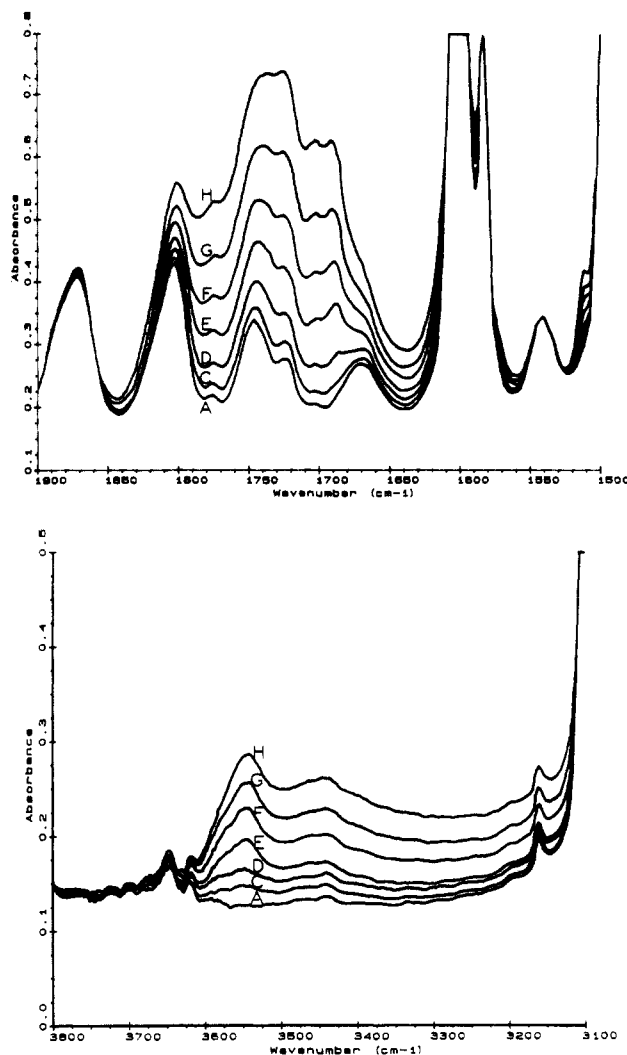


Figure 1. Evolution of the IR spectra of a polystyrene film (thickness $89 \mu\text{m}$): on irradiation at $\lambda \geq 300 \text{ nm}$, 60°C : (A) 0 h; (C) 90 h; (D) 150 h; (E) 182 h; (F) 217 h; (G) 257 h; (H) 294 h. (Top (a)) carbonyl vibration region; (bottom (b)) hydroxyl vibration region.

oxidized polyolefins.²³ The acyl fluorides formed by reaction of carboxylic acid with SF_4 are characterized by a distinct $\text{C}=\text{O}$ absorption above 1800 cm^{-1} . The SF_4 reaction has also been shown to give a total disappearance of OH absorption.²³

Treatment by SF_4 carried out on photooxidized polystyrene films led to a decrease of the carbonyl absorption, and new absorption bands appeared at 1813 and 1841 cm^{-1} (Figure 3). Although some data on the IR absorptions of acyl fluorides were available in the literature, we had to compare model compounds in solution in hexane or hexadecane since some matrix effects could be suspected. In addition, some model compounds were introduced in polystyrene films by permeation and then submitted to SF_4 for 1 h. Table I shows the results of the derivatization reaction and compares them to those obtained for SF_4 reactions on the model compounds introduced in a polypropylene matrix. The results obtained with polypropylene are in good concordance with the literature.²³ Our results show the effects of the polymer matrix on the position of the absorption maxima of the carboxylic acids and their derivatives.

Figure 3 also shows a decrease of the absorption bands of the photoproducts that react with SF_4 at 1698 , 1710 , and 1732 and a shoulder at 1753 cm^{-1} . Comparison of the evolutions of the spectra after SF_4 treatment with the results given in Table I leads to the following conclusions:

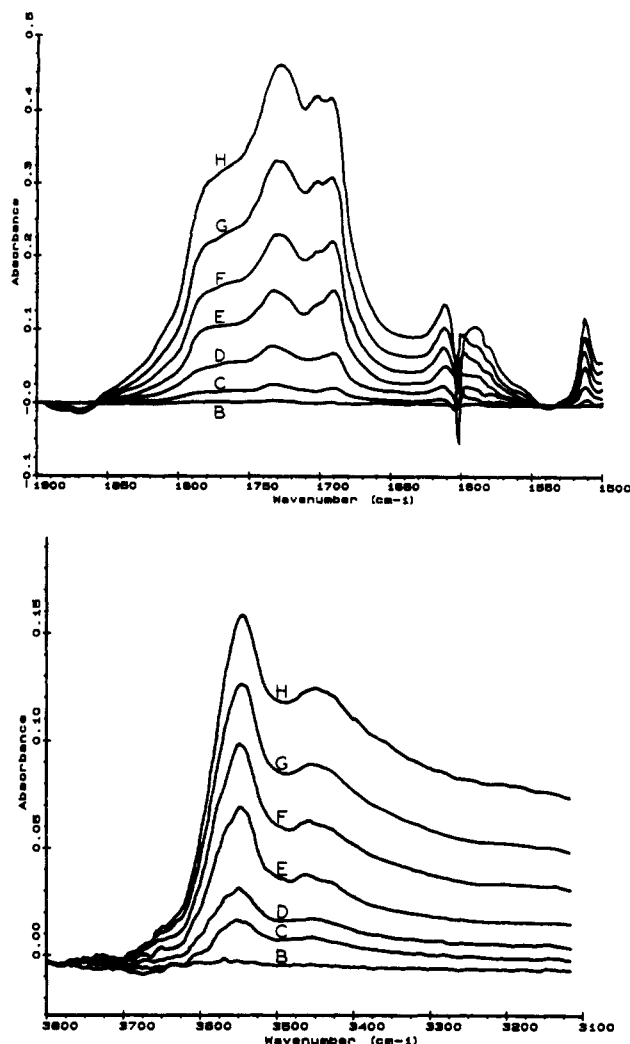


Figure 2. Subtracted spectra between the nonirradiated and the irradiated sample for various irradiation times ($\lambda \geq 300$ nm, 60°C): (B) 25 h; (C) 90 h; (D) 150 h; (E) 182 h; (F) 217 h; (G) 257 h; (H) 294 h. (Top (a)) carbonyl vibration region; (bottom (b)) hydroxyl vibration region.

(i) The absorption maximum at 1698 cm^{-1} is assigned to the dimer form of benzoic acid, which reacts with SF_4 to give the absorption maximum at 1813 cm^{-1} . (ii) The absorption maximum at 1710 cm^{-1} is assigned to the formation of a dimer carboxylic acid $-\text{CH}_2\text{COOH}$. The reaction with SF_4 gives the acyl fluoride $-\text{CH}_2\text{COF}$ at 1841 cm^{-1} . (iii) No carboxylic acid chain group with the structure $-\text{CH}(\text{Ph})\text{COOH}$ is formed since there is no absorption of the derivation product at 1837 cm^{-1} .

By analogy with recent findings in polypropylene photooxidation,²⁴ the maxima at 1732 and 1753 cm^{-1} are respectively assigned to monomeric forms of benzoic acid and chain acid $-\text{CH}_2\text{COOH}$ associated with hydroxylated groups.

The analysis of the subtraction of spectra shows that, after SF_4 treatment, several bands remain with maxima at 1690 , 1725 , 1732 , and 1785 cm^{-1} . The absorption in the domain 3600 – 3100 cm^{-1} was almost completely lost (Figure 3).

Ammonia Reactions. Reaction of photooxidized polystyrene films with ammonia led to the decrease of the carbonyl bands between 1680 and 1800 cm^{-1} and to an increase of absorbance between 1680 and 1500 cm^{-1} (Figure 4). In the domain 3800 – 3000 cm^{-1} , no useful information is obtained since the changes observed correspond to the formation of a broad band between 3400 and 3000 cm^{-1} without any definite maximum. The subtraction of spectra

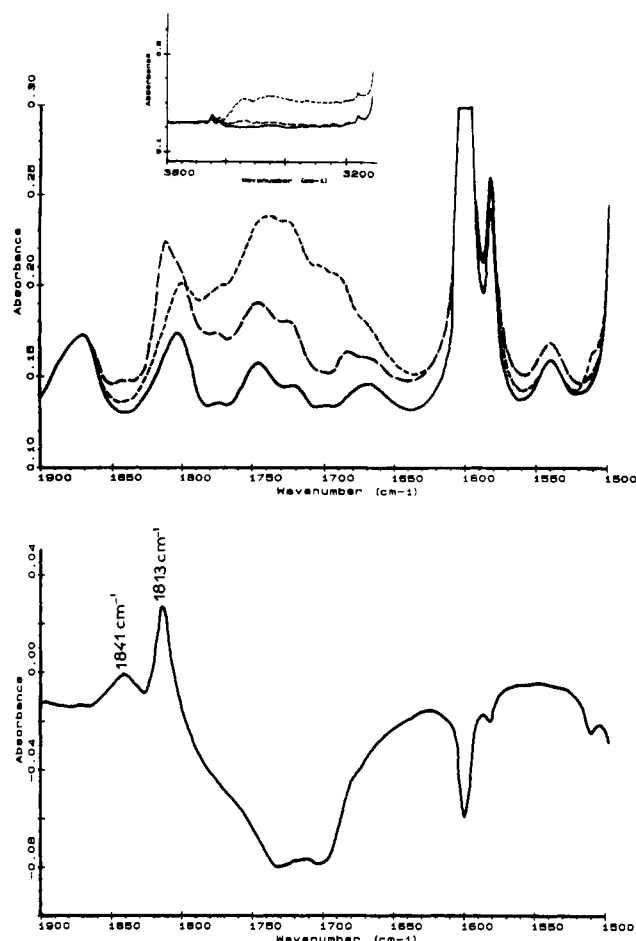


Figure 3. Evolution of the IR spectra after SF_4 treatment of a photooxidized film (thickness $16\text{ }\mu\text{m}$). (Top (a)) carbonyl vibration region: (—) 0 h; (---) 123 h; (---) SF_4 treated, 22 h. The inset shows the hydroxyl vibration region. (Bottom (b)) subtracted spectrum between the irradiated and the treated film in the carbonyl vibration region.

Table I
IR Absorption of Carboxylic Acids and Corresponding Acyl Fluorides

model compd	$\bar{\nu}_{\text{CO}^{\text{max}}}, \text{cm}^{-1}$			
	in polystyrene		in polypropylene	
	before SF_4	after SF_4	before SF_4	after SF_4
acetic acid			1717	1848
hexanoic acid	1709	1841	1715	1847
2-phenylbutyric acid	1706	1837	1710	1840
benzoic acid	1698	1813	1700	1818

recorded in the 1900 – 1500 cm^{-1} region shows that the decrease of the carbonyl band corresponds to the decrease of three main maxima at 1698 , 1732 , and 1785 cm^{-1} . However, the shape of the whole band shows that the other maxima at 1710 and 1753 cm^{-1} are involved in the decrease of the carbonyl band.

The increase of absorbance between 1680 and 1500 cm^{-1} reveals maxima at 1553 and 1592 cm^{-1} and a maximum at 1668 cm^{-1} . The absorption maximum at 1553 cm^{-1} corresponds to the $\text{C}=\text{O}$ band of the carboxylate ion obtained by neutralization of benzoic acid by ammonia (comparison was made with benzoic acid introduced into a polystyrene sample and then treated with NH_3). The formation of this band parallels the decrease of the band at 1698 cm^{-1} and part of the band at 1732 cm^{-1} .

An ammonia treatment carried out on the corresponding model compound shows that the neutralization of a carboxylic acid group $-\text{CH}_2\text{COOH}$ (corresponding in the

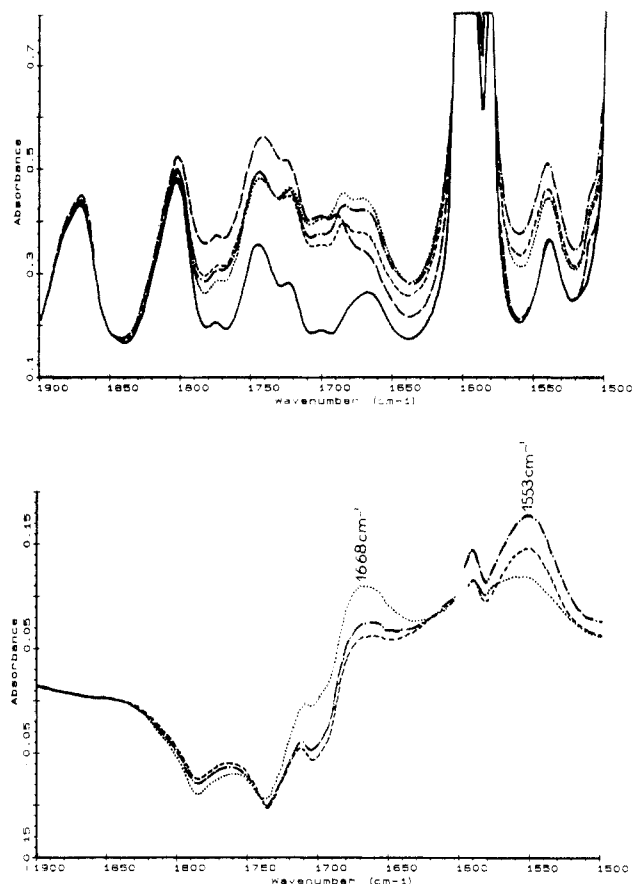


Figure 4. Evolution of the IR spectra (carbonyl vibration region) of a photooxidized film (thickness 117 μm) treated by NH_3 . (Top (a)) Irradiation time: (—) 0 h; (---) 174 h, NH_3 treatment time: (- · -) 1.3 h; (- · ·) 3.5 h; (···) 31 h. (Bottom (b)) Subtracted spectra between the irradiated and the treated film during various durations: (- · -) 1.3 h; (- · ·) 3.5 h; (···) 31 h.

photooxidized sample to the absorption maxima at 1710 and 1753 cm^{-1} gives a carboxylate ion with a $\text{C}=\text{O}$ band at 1585 cm^{-1} . However, such a maximum is not observable in the IR spectrum of the treated sample since the residues of the intense absorptions at 1600/1583 cm^{-1} mask this band.

The maximum at 1668 cm^{-1} that appears after the reaction with ammonia is assigned to the $\text{C}=\text{O}$ stretching vibration of an amide group. Formation of this absorption band parallels the decrease of the bands at 1785 and 1732 cm^{-1} . The maximum at 1732 cm^{-1} was assigned above to a monomeric form of benzoic acid associated to hydroxylated compounds, but the decrease of this band is too important to be assigned only to the associated acid. A second product, neutralized by NH_3 and not by SF_6 , has to be proposed. Ester groups absorb in this region, and it is well-known that they react irreversibly with ammonia to give amide groups.²² The formation of ester groups absorbing in the range 1730–1735 cm^{-1} is often proposed to explain the photooxidation of many polymers. However, molecular esters introduced in polystyrene show little reactivity with ammonia. Attribution of the maximum at 1732 cm^{-1} to a δ -lactone seems more reasonable since δ -valerolactone introduced into polystyrene reacts more rapidly with NH_3 and gives a δ -lactam ($\nu_{\text{C}=\text{O}} = 1668 \text{ cm}^{-1}$).

From comparison with the model compound, the maxima at 1785 and 1725 cm^{-1} are assigned to benzoic anhydride, whose reaction with NH_3 gives an amide (1668 cm^{-1}) and a carboxylate ion (1553 cm^{-1}).²²

After the reaction with NH_3 , the IR spectra of treated samples show that a broad band remains with maxima at

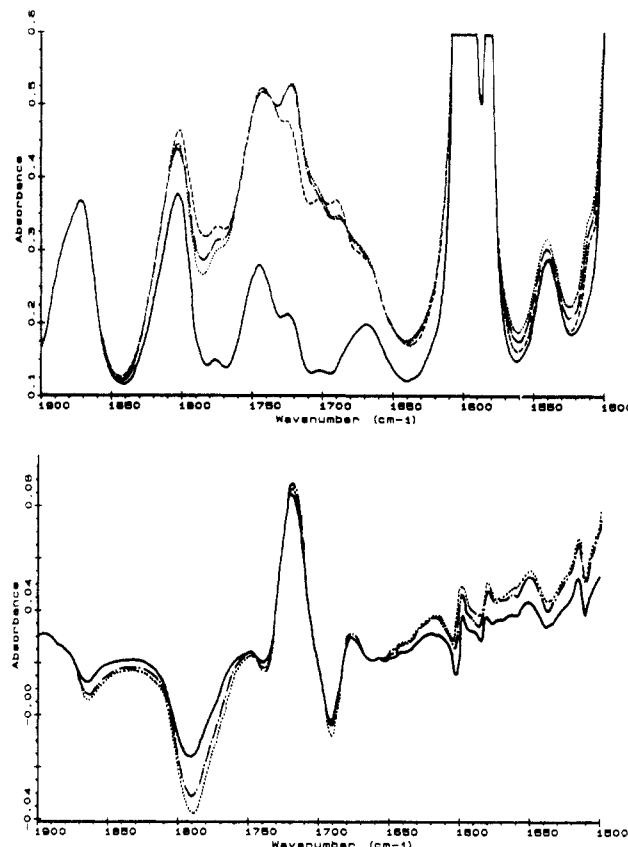


Figure 5. Evolution of the IR spectra (carbonyl vibration region) of a photooxidized film (thickness 100 μm) treated by methanol. (Top (a)) Irradiation time: (—) 0 h; (---) 177 h. Methanol treatment time: (- · -) 21 h; (···) 77 h. (Bottom (b)) Subtracted spectra between the irradiated and the treated film during various durations: (—) 21 h; (---) 42 h; (···) 77 h.

1690 and 1725 cm^{-1} that correspond to unreacted products: aromatic ketone $-\text{CH}_2\text{C}(\text{O})\text{Ph}$ and aliphatic ketone $-\text{CH}_2\text{C}(\text{O})\text{CH}_2-$.

Methanol Treatment. Immersion of photooxidized films in methanol for ca. 80 h led to some changes of the IR spectra of the so-treated films (Figure 5). In the subtracted spectra it is observed that the absorption bands with maxima at 1690, 1698, 1732, and 1785 cm^{-1} decrease and that an absorption band at ca. 1720 cm^{-1} increases. These observations may be interpreted as follows:

(i) Benzoic acid (1698/1732 cm^{-1}) is soluble in methanol and partly extracted by the solvent.

(ii) The absorption at 1690 cm^{-1} is usually assigned to the $\text{C}=\text{O}$ stretching vibration of aromatic ketones. The decrease of the band at 1690 cm^{-1} shows that at least part of this absorption band has to be assigned to a low molecular weight compound, which will be identified later as acetophenone. The residual absorption is then assigned to an end-chain aromatic ketone.

(iii) The decrease of the intensity at 1785 cm^{-1} is correlated to the increase of the absorption at 1720 cm^{-1} . The alcoholysis of benzoic anhydride gives an ester of 1720 cm^{-1} (methyl benzoate) and benzoic acid.²²

Identification of the Products by Physical Treatment. Thermolysis of Photooxidized Samples. Thermolysis in vacuum of photooxidized samples were carried out at several temperatures, 60, 80 and 100 $^{\circ}\text{C}$. No modification of the IR spectra of the polystyrene films was observed even after hundreds of hours of treatment at 60 or 80 $^{\circ}\text{C}$. At 100 $^{\circ}\text{C}$, slight changes were observed in the 1900–1500 cm^{-1} domain: intensity of the maxima at 1690, 1698, 1704, 1710, and 1732 cm^{-1} decrease, indicating a loss of some molecular compounds. These

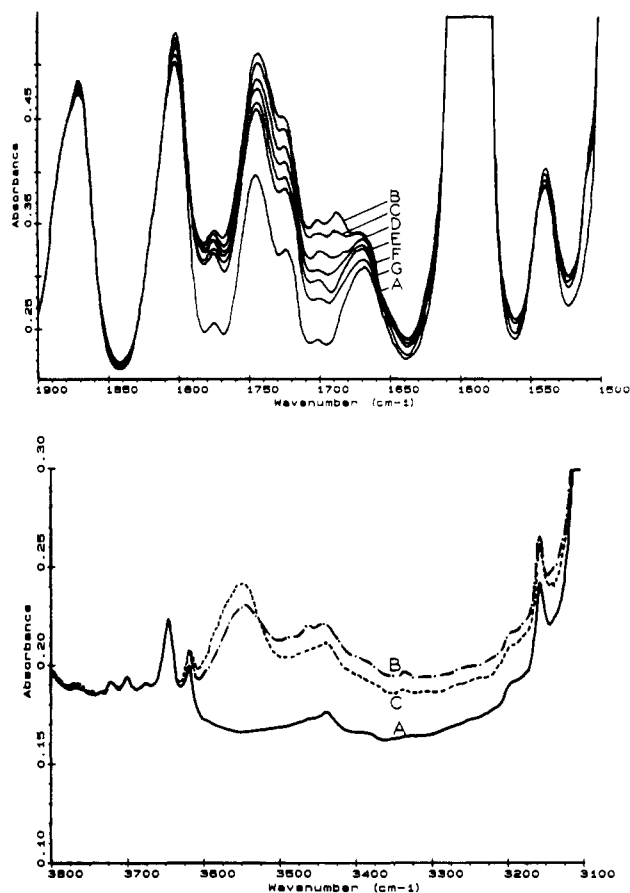


Figure 6. Evolution of the IR spectra of a polystyrene film (thickness 105 μm) photooxidized for 221 h (B) and then photolyzed ($\lambda \geq 300$ nm) for (C) 199 h, (D) 367 h, (E) 531 h, (F) 739 h, and (G) 950 h. Spectrum A is the initial spectrum. (Top (a)) carbonyl vibration region; (bottom (b)) hydroxyl vibration region.

compounds have been identified to benzoic acid (1698/1732 cm^{-1}) and to an aromatic ketone (1690 cm^{-1}) (acetophenone).

In the 3800–3200 cm^{-1} domain, a decrease of the absorption is observed, that is attributed to a loss of the OH absorption of benzoic acid, and to an homolysis of hydroperoxides which are formed in associated forms and present a broad band with a maximum between 3300 and 3400 cm^{-1} .

Photolysis of Photooxidized Samples. Polystyrene films photooxidized for 211 h were submitted to photolysis in the absence of oxygen in the SEPAP 12-24 unit. In the 1900–1500- cm^{-1} domain, a decrease of absorbance is observed that involves all the maxima (Figure 6a). Differences appear, however, between photolysis and thermolysis of photooxidized samples since the decrease of the ketone at 1690 cm^{-1} is more important in photolysis. This result confirms that part of the absorption at 1690 cm^{-1} is due to a chain product, e.g., an aromatic ketone end group $-\text{CH}_2\text{C}(\text{O})\text{Ph}$.

In the hydroxyl domain (Figure 6b), a decrease of the broad band between 3500 and 3100 cm^{-1} and an increase of the narrow band at 3540 cm^{-1} are observed. An invariant state is observed after 200 h (in the carbonyl domain, no stationary state was reached even after 900 h). The decrease of the broad absorption band is attributed to the photolysis of hydroperoxides (3450 cm^{-1}).

Photolysis of hydroperoxides leads to an increase of the absorption of hydroxyl groups: $-\text{CH}_2\text{C}(\text{OH})(\text{Ph})\text{CH}_2-$, 3540 cm^{-1} (comparison with the model compound $\text{CH}_3\text{C}(\text{OH})(\text{Ph})\text{CH}_3$ confirms this assignment). The increase

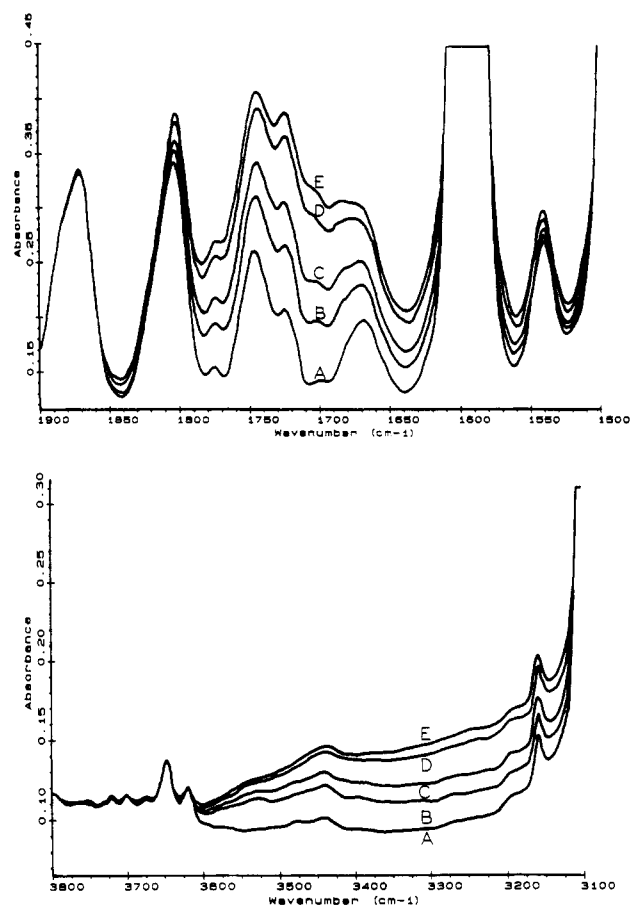


Figure 7. Evolution of the IR spectra of a polystyrene film (thickness 75 μm) on irradiation at $\lambda = 253.7$ nm, 30 $^{\circ}\text{C}$: (A) 0 h; (B) 23 h; (C) 49 h; (D) 97 h; (E) 140 h. (Top (a)) carbonyl vibration region; (bottom (b)) hydroxyl vibration region.

of the band at 3540 cm^{-1} can also be assigned in part to a photoreduction of the ketonic groups $-\text{CH}_2\text{C}(\text{O})\text{Ph}$.

2. Photooxidation at "Short Wavelength" ($\lambda = 253.7$ nm). Figure 7 shows the IR spectrum of a polystyrene film (thickness 75 μm) irradiated under the standard conditions of the SEPAP 253.7 unit (temperature 30 $^{\circ}\text{C}$) in the presence of air.

Subtractions of spectra recorded in the domain 1900–1500 cm^{-1} show that the photooxidation at 253.7 nm leads to the formation of a broad absorption band centered around 1710 cm^{-1} and presenting several maxima or shoulders: 1690, 1710, 1725, and 1785 cm^{-1} (Figure 8). A weak isolated band at 1515 cm^{-1} and a band centered around 1605 cm^{-1} are also observed.

The broad band at 1710 cm^{-1} appears different from that observed for long-wavelength irradiation. However, this band will be shown to result from the same photoproducts but with different relative concentrations.

In the region 3800–3000 cm^{-1} , a broad hydroxyl absorption band develops: in contrast to the hydroxyl absorption observed before for long-wavelength irradiation, maxima are not easily discerned, but comparison of both evolutions shows that maxima at 3540, 3450, and 3250 cm^{-1} are certainly present in this broad absorption band. The photoproduct corresponding to the absorption at 3540 cm^{-1} is formed at a lower concentration.

Identification of the Photoproducts by Derivatization Reactions. Reaction of photooxidized PS films with SF_4 or NH_3 led to similar changes to those reported above for samples photooxidized at long wavelengths ($\lambda \geq 300$ nm). The only noticeable difference was that the contribution of the photoproducts at 1710 cm^{-1} was much higher for irradiation at short wavelength.

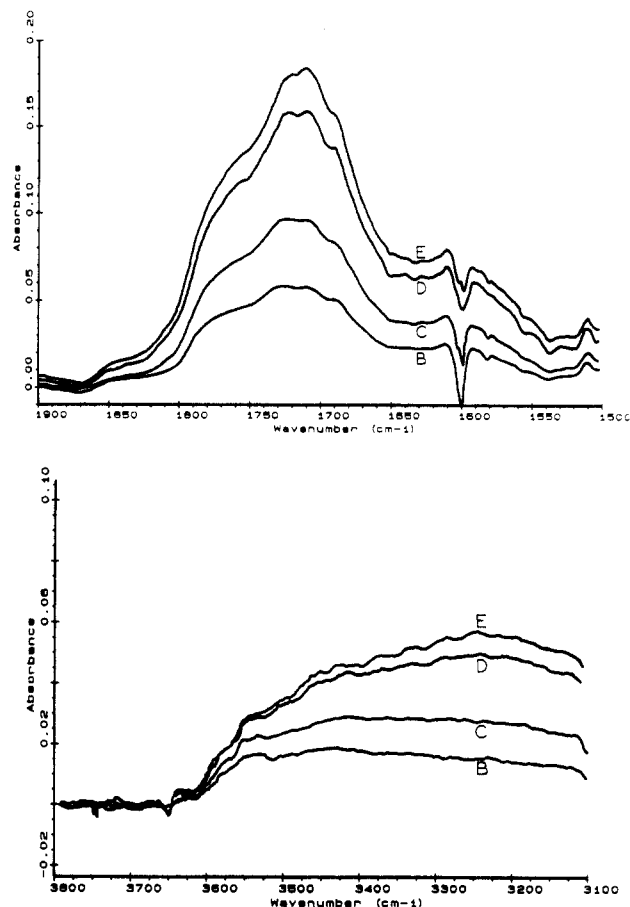


Figure 8. Subtracted spectra between the nonirradiated and the irradiated ($\lambda = 253.7$ nm, 30°C) film for various irradiation times: (B) 23 h; (C) 49 h; (D) 97 h; (E) 140 h. (Top (a)) carbonyl vibration region; (bottom (b)) hydroxyl vibration region.

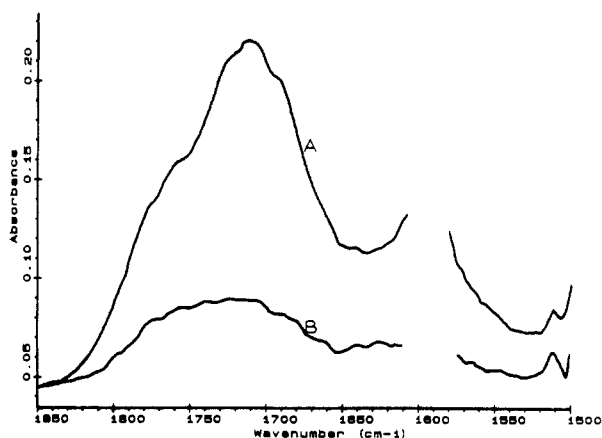


Figure 9. Subtracted spectra (A) between the nonirradiated and the irradiated film ($\lambda = 253.7$ nm, 30°C , 232 h) and (B) between the nonirradiated and the irradiated and methanol-treated film (7.5 h). Film thickness $177\ \mu\text{m}$.

Methanol Treatment. HPLC Analysis of the Extract. Immersion in methanol of photooxidized polystyrene films led to an important decrease of absorbance of the photooxidation products after a few hours in the solvent.

In the domain of carbonylated product absorption, a broad band with a low intensity remains after treatment (Figure 9), centered around $1725\ \text{cm}^{-1}$.

In the $3800\text{--}3100\text{-cm}^{-1}$ domain, a decrease of the bands at 3250 and $3450\ \text{cm}^{-1}$ is observed. The weak band at $3540\ \text{cm}^{-1}$ is not observed to decrease during the treatment by methanol. In the whole range of IR investigations ($4000\text{--}400\ \text{cm}^{-1}$), no new absorption band due to reactions with

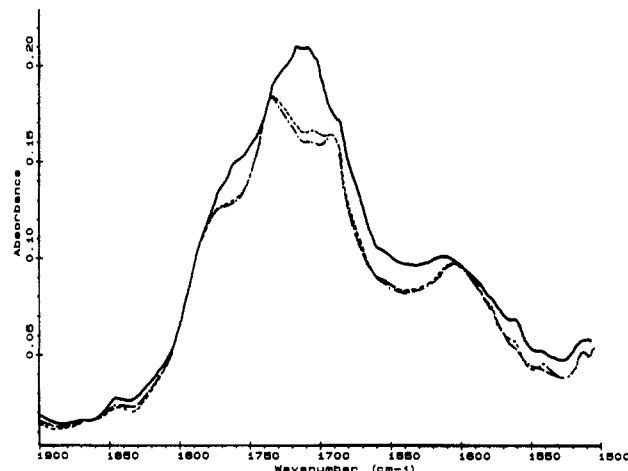


Figure 10. Subtracted spectra between the nonirradiated and the irradiated film ($\lambda = 253.7$ nm, 30°C , (—) 200 h) and between the nonirradiated and the irradiated and thermolyzed film (100°C , (- - -) 40 h, (- · -) 205 h).

methanol appears. The absorption bands that disappeared correspond then to photoproducts that have been extracted by the solvent.

Before commenting on the nature of the evolution of the IR spectra due to the MeOH treatment, we report on the results of the HPLC analysis of the solvent.

The chromatogram of the methanol used to extract some of the oxidation photoproducts from polystyrene films photooxidized at 253.7 nm shows several peaks. The UV-visible spectra of each fraction recorded in the range $200\text{--}500$ nm were compared to the spectra of some model compounds analyzed under the same conditions. Retention times and UV-visible spectra were exactly fitting for most of them: benzoic acid, acetophenone, benzaldehyde, methyl benzoate, and styrene monomer were observed among the extracted products. Some nonaromatic photoproducts absorbing at wavelengths below 200 nm were observed but not identified. An aromatic photoproduct presenting absorption maxima at 340 , 355 , and 375 nm was observed. Comparison with a model compound, dibenzoylmethane ($\text{PhC(O)CH}_2\text{C(O)Ph}$), gave an acceptable fit in terms of both retention time and UV-visible spectra. These identifications correspond to the attributions deduced from the derivatization reactions and the physical treatments.

The decrease of absorbance recorded in the C=O region of the IR spectra of the so-treated films is then attributed to the extraction of molecular products: benzoic acid ($1698/1732\ \text{cm}^{-1}$), benzophenone ($1690\ \text{cm}^{-1}$), benzaldehyde ($1704\ \text{cm}^{-1}$), benzoic anhydride ($1785/1725\ \text{cm}^{-1}$) (which leads to methyl benzoate), and dibenzoylmethane ($1515/1605\ \text{cm}^{-1}$). The broad absorption that remains after the treatment corresponds to the chain products C(O)Ph ($1690\ \text{cm}^{-1}$), CH_2COOH ($1710\text{--}1753\ \text{cm}^{-1}$), δ -lactone ($1732\ \text{cm}^{-1}$), and chain ketone ($1725\ \text{cm}^{-1}$). In the domain of hydroxyl compounds, the broad band at $3250\ \text{cm}^{-1}$ of dimer carboxylic acids decreases whereas the narrow band at $3540\ \text{cm}^{-1}$ of monomer hydroxyl $\text{CH}_2\text{C(OH)(Ph)CH}_2\text{--}$ remains unchanged.

Identification of the Photoproducts by Physical Treatment. Thermolysis of Photooxidized Samples. Thermolysis at 100°C under vacuum of photooxidized films led to a decrease of absorbance of the carbonylated and hydroxylated photoproducts. After 40 h of thermolysis the absorbance remains constant. The subtractions of spectra show that the decrease of absorption bands with maxima at 1710 and $1753\ \text{cm}^{-1}$ is responsible for the

Table II
Characteristics Absorptions of the Photoproducts and Their Identification Methods

photoproduct		model compd ^{a-e} $\bar{\nu}$ (cm ⁻¹)	deriv reacn	phys treatment
structure	$\bar{\nu}$ (cm ⁻¹)			
PhC(O)CH ₂ -	1690	1690 ^a		photolysis
PhC(O)CH ₃	1690	1690		MeOH/HPLC, photolysis, thermolysis
PhCOOH dimer	1698	1698	SF ₄ , 1813 cm ⁻¹	MeOH/HPLC, thermolysis
associated form	1732		NH ₃ , 1553 cm ⁻¹	
PhCHO	1704	1704		MeOH/HPLC, thermolysis
-CH ₂ COOH	1710	1710 ^b	SF ₄ , 1841 cm ⁻¹	
associated form	1753		NH ₃ , 1585 cm ⁻¹	
CH ₃ COOH	1710	1710		thermolysis
HCOOH	1710	1710		thermolysis
-CH ₂ C(O)CH ₂ -	1725	1725 ^c		
δ -lactone	1732	1732 ^d	NH ₃ , 1668 cm ⁻¹	
PhC(O)OC(O)Ph	1785	1785	NH ₃ , 1668, 1553 cm ⁻¹	
	1725	1725	MeOH, 1720 cm ⁻¹	
-COOH dimer	3250	3250 ^b		
-OH dimer	3450	3450		
-OOH dimer	3450	3450		photolysis, thermolysis
-CH ₂ C(OH)(Ph)CH ₂ -	3540	3540 ^e		

^{a-e} Model compounds: (a) acetophenone, (b) hexanoic acid, (c) 3-heptanone, (d) δ -valerolactone, (e) 2-phenyl-2-propanol.

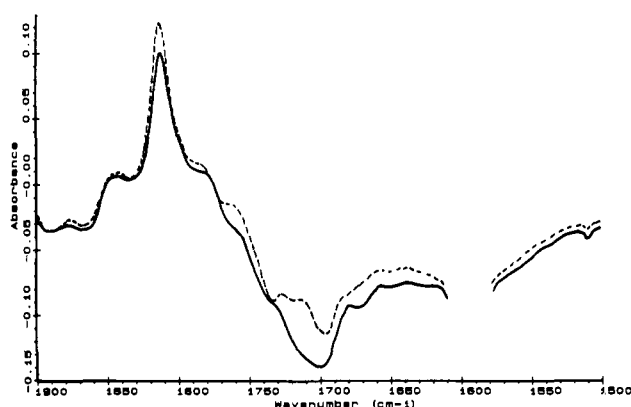


Figure 11. SF₄ treatment: (—) subtracted spectrum between the irradiated ($\lambda = 253.7$ nm, 30 °C, 180 h) and SF₄-treated film (24 h); (---) subtracted spectrum between the irradiated ($\lambda = 253.7$, 30 °C, 180 h) and thermolyzed (100 °C, 88 h) and SF₄-treated film (24 h).

evolution of the IR spectra in the domain of analysis of carbonylated photoproducts (Figure 10). Maxima of the broad bands at 3250 and 3450 cm⁻¹ decrease in the domain of OH vibrations.

To analyze the photoproducts that disappear during the thermolysis, an analysis of the gas phase was carried out: a large sheet of polystyrene film first photooxidized for 200 h at 253.7 nm was rolled and placed into a gas cell consisting of a glass cylinder whose ends were KBr windows. The cylinder was then sealed under vacuum and placed in an oven at 100 °C. The gas phase in the cell was then analyzed by IR spectroscopy. The spectra that were recorded showed an intense absorption in the 1900–1500-cm⁻¹ domain with a main maximum at 1733 cm⁻¹ and two weaker bands at 1776 and 1797 cm⁻¹. These maxima, as well as the absorption bands in the other domains of the IR range, fitted with those of gaseous acetic and formic acids (ν_{CO} respectively 1733/1776 cm⁻¹ for acetic acid dimer/monomer and 1733/1797 cm⁻¹ for formic acid dimer/monomer). These identifications were in agreement with the observations reported on the evolution of IR spectra of the so-treated films since the maximum that was observed to decrease corresponded to the dimer form of acetic and formic acids trapped in the polymer matrix. This confirms the assignment of the bands at 1710 and 1753 cm⁻¹ respectively to the dimer and the hydroxyl-associated forms of acetic and formic acids.

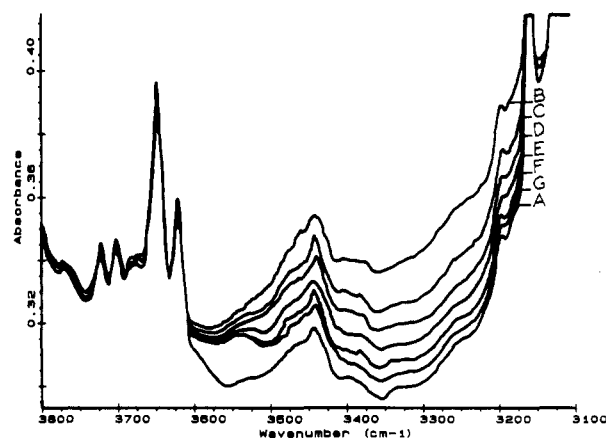
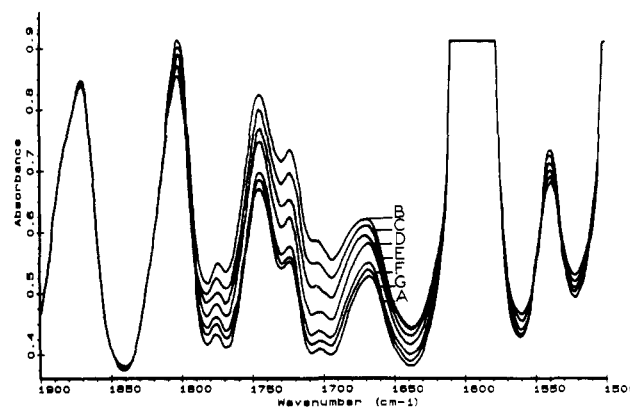


Figure 12. Evolution of the IR spectra during photolysis ($\lambda = 253.7$ nm, 30 °C) of a polystyrene film (thickness 203 μ m) photooxidized at $\lambda = 253.7$ nm, 30 °C. Irradiation time: (A) 0 h; (B) 135 h. Photolysis time: (C) 10 h; (D) 110 h; (E) 235 h; (F) 600 h; (G) 1045 h. (Top (a)) carbonyl vibration region; (bottom (b)) hydroxyl vibration region.

A further confirmation of the acidic nature of the products that diffused out of the sample in thermolysis was given by the evolution of a pH paper introduced in the cell before the treatment, revealing that acidic media were formed in the gas phase.

Furthermore, treatment of thermolyzed films with SF₄ confirmed this evolution. Figure 11 compares the IR spectrum (1900–1500 cm⁻¹) of a film photooxidized and then thermolyzed with the IR spectrum of a film that had been only photooxidized. It is observed in this figure that the subtraction between the species corresponds to the

disappearance of the acidic products during the thermolysis.

Photolysis of Photooxidized Samples. Irradiation of photooxidized samples sealed under vacuum in quartz tubes was performed at 253.7 nm. The IR analysis of the photolyzed films showed that, after ca. 1000 h of irradiation, almost all the oxidation photoproducts had disappeared and the initial absorption spectrum of polystyrene was recovered except in the OH domain, where the narrow band at 3540 cm^{-1} remained (Figure 12). This observation confirms that the OH absorption at 3540 cm^{-1} has to be assigned to free hydroxyl groups.

This unusual behavior shows that most of the photoproducts formed on photooxidation of polystyrene are low molecular weight compounds or are so oxidized that their photolysis leads to molecular products that can diffuse easily out of the polymer matrix.

Conclusion

By coupling spectrophotometric and chromatographic analyses with experiments including chemical and physical treatments carried out on polystyrene films photooxidized at long wavelengths ($\lambda \geq 300\text{ nm}$) or short wavelength ($\lambda = 253.7\text{ nm}$), the photoproducts observed by IR spectroscopy have been identified. The same products are formed in both conditions of irradiation but their relative concentrations are different. Table II gives the characteristic absorptions of these photoproducts and the methods which have permitted their identification.

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Registry No. PS, 9003-53-6; SF₄, 7783-60-0; NH₃, 7664-41-7; acetic acid, 64-19-7; hexanoic acid, 142-62-1; 2-phenylbutyric acid, 90-27-7; benzoic acid, 65-85-0; methanol, 67-56-1.