Macromolecules **1992,** *25,* 4127–4133

Polystyrene Photooxidation. 2. A Pseudo Wavelength Effect

Bénédicte Mailhot and Jean-Luc Gardette*

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

Received December 10, 1991; Revised Manuscript Received March 12, 1992

ABSTRACT: The photoproducts formed in polystyrene photooxidized by exposure to long wavelengths ($\lambda \geq 300$ nm) or short wavelength ($\lambda = 253.7$ nm) absorbing in the IR range were identified and reported in the preceding paper. It was shown that, despite some differences in the distribution of oxidation photoproducts, the same products were obtained. The present paper reports on complementary experiments carried out at a different temperature and on microspectrophotometric determination of the photoproduct profiles. The apparent differences resulting from the short- or long-wavelength irradiation are attributed to the diffusion of the low molecular weight photoproducts. A general mechanism accounting for the photooxidation of the polystyrene at short or long wavelengths is given.

Introduction

In the preceding paper,[1] we showed that the oxidation photoproducts detected by IR spectroscopy of polystyrene (PS) films photooxidized at short wavelength ($\lambda = 253.7$ nm) or long wavelengths ($\lambda \geq 300$ nm) could be studied by coupling IR spectroscopy and derivatization reactions or physical posttreatments. The different products formed were identified, and it was shown that the photoproducts obtained under both conditions of irradiation were similar, but accumulated at different relative concentrations.

In the present paper we account for the different distributions of the photoproducts depending on the irradiation conditions.

Experimental Section

Most experimental techniques have already been described.[1] For the preparation of thin films (thickness 5–10 μm), polystyrene films (100–200 μm) from CdF Chimie (see paper 1) were dissolved in toluene and then purified by reprecipitation from methanol. The purified PS was dried under vacuum for 48 h. Polymer thin films were cast from a methylene chloride solution on KBr windows, the methylene chloride being removed under vacuum for 24 h. The phenyl band (1583 cm^{-1}) was used to determine the sample thickness.

Irradiations of polystyrene films at long-wavelengths and 30 °C were carried out in a SEPAP 14-24. This apparatus has been described elsewhere.[2] The light source is the same as the source of the SEPAP 12-24 used for irradiations at long wavelenths ($\lambda \geq 300$ nm) at 60 °C.

Measurements of oxidation photoproduct profiles in photooxidized films were carried out by a technique described earlier.[3] Measurements were performed on a Nicolet 800 equipped with a NICPLAN microscope (liquid nitrogen-cooled MCT detector, 128 scan summations). The films were embedded in an epoxy resin after irradiation and then sliced with a Reichert and Jung microtome. Slices with a thickness of ca. 100 μm were obtained and then examined through the FTIR microscope (Figure 1). The profile of the relative concentration of the oxidation photoproducts formed in the film may then be determined with a fairly good accuracy.

ATR spectra were recorded using a KRS-5 (45°) crystal (200 scan summations).

Experimental Results

1. Photooxidation at Long Wavelengths ($\lambda \geq 300$ nm) at 30 °C. The evolution of the IR spectra of polystyrene films (thickness 190 μm) submitted to photooxidation in the SEPAP 14-24 unit at 30 °C is presented in Figures 2 and 3. We note the following:

(i) The carbonyl band between 1900 and 1650 cm^{-1} presents several maxima or shoulders: 1690, 1698, 1732, and 1785 cm^{-1}. This broad band results from the convolution of several bands that have been identified by chemical and physical treatments similar to those reported in paper 1 for photooxidation at long wavelengths and 60 °C.

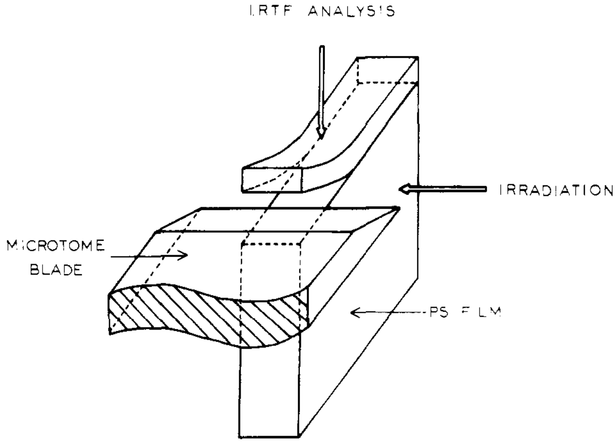


Figure 1. Experimental method for analysis of the polymer films by the microspectrophotometric technique.

(ii) In the 3800–3000-cm^{-1} domain, a band with a maximum at 3540 cm^{-1} is observed. Two broad bands with maxima at 3450 and 3250 cm^{-1} are also observed to increase.

Although the shapes of the bands were slightly different from those recorded under the conditions of irradiation at 60 °C, these bands were shown to result from the same photoproducts. Only the relative concentrations were different. Assignments of the different maxima are given in Table I.

2. Determination of the Photoproduct Profiles. The measurements of the distribution of photoproducts through the polymer along the irradiation axis were made for irradiations in the SEPAP 12-24 unit (60 °C) and the SEPAP 253.7 unit (30 °C).

For long-wavelength irradiation, measurements were carried out on sample of 240-μm thickness irradiated for 177 and 199 h. As explained in the Experimental Section, irradiated films were embedded in an epoxy resin and thin slices of 100-μm thickness were then analyzed. IR spectra were recorded every 20 μm, and the absorbance (OD) at 1725 cm^{-1} was measured on each spectrum.

The evolutions of OD(1725 cm^{-1}) as a function of the depth at which the spectra were recorded is shown on Figure 4. The concentration gradients which are observed are rather symmetrical; that means that since the sample

0024-9297/92/2225-4127$03.00/0

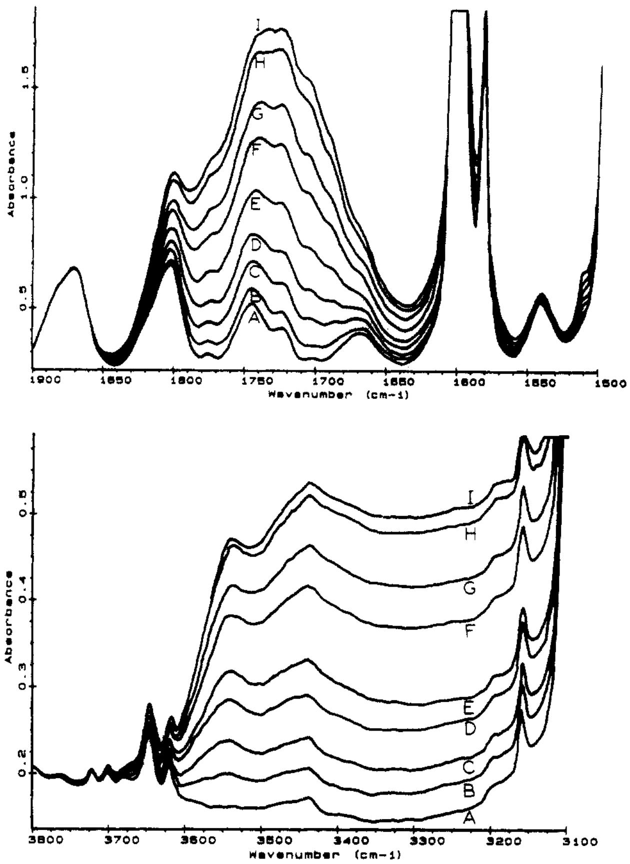


Figure 2. Evolution of IR spectra of a polystyrene film (thickness 194 μm) photooxidized for (B) 264, (C) 373, (D) 461, (E) 559, (F) 653, (G) 729, (H) 823, and (I) 895 h (λ ≥ 300 nm, 30 °C). Spectrum A is the initial spectrum. (Top (a)) Carbonyl vibration regions; (bottom (b)) hydroxyl vibration region.

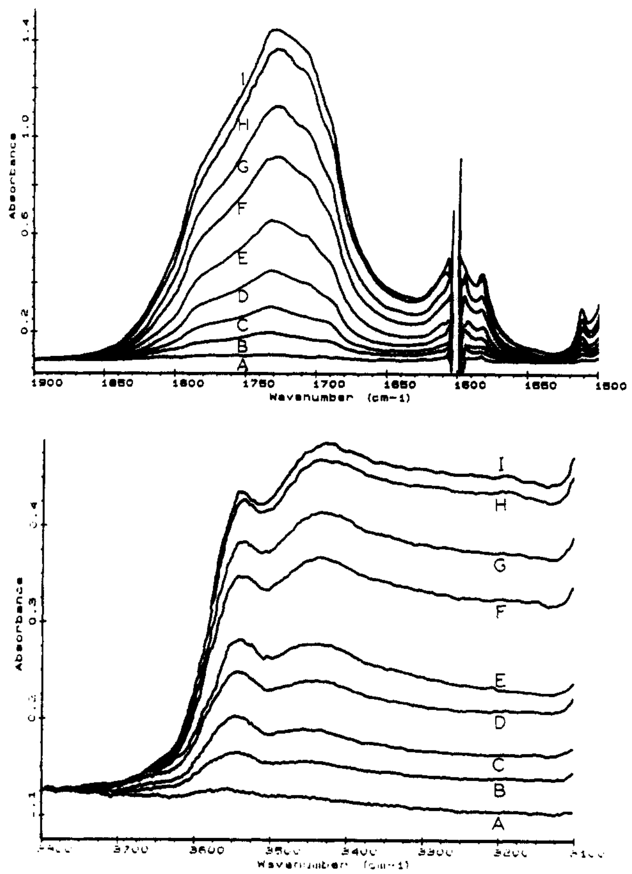


Figure 3. Subtracted spectra between the nonoxidized film and the film photooxidized for (A) 65, (B) 264, (C) 373, (D) 461, (E) 559, (F) 653, (G) 729, (H) 823, and (I) 895 h (λ ≥ 300 nm, 30 °C). (Top (a)) carbonyl vibration region; (bottom (b)) hydroxyl vibration region.

Table I
Photooxidation Products of Polystyrene

photoproduct	$\bar{\nu}$ (cm^{-1})	photoproduct	$\bar{\nu}$ (cm^{-1})
$PhC(O)CH_2$–	1690	–$CH_2C(O)CH_2$–	1725
$PhC(O)CH_3$	1690	δ-lactone	1732
PhCOOH dimer	1698	PhC(O)OC(O)Ph	1785
associated form	1732		1725
PhCHO	1704	–COOH dimer	3250
–CH_2COOH	1710	–OH dimer	3450
associated form	1753		
HCOOH	1710	–OOH dimer	3450
CH_3COOH	1710	–$CH_2C(OH)(Ph)CH_2$–	3540

is transparent to the incident light, the rear of the film is as photooxidized as the front side. The shape of the gradient shows that the core of the film is almost as oxidized as the front and rear layers. This result is important for comprehension of the behavior of films irradiated at long-wavelengths, and it points out that the oxidation photoproducts are homogeneously dispersed through the irradiated films.

Such a behavior of polystyrene is explained by considering the relatively important permeability of the polymer to oxygen and a weak reactivity in these conditions of irradiation since the intrinsic absorption of long wavelengths is low.

Concentration profiles were also determined for polystyrene films (thickness 100 μm) irradiated at 253.7 nm (slices of 90-μm thickness). Measurements were made on bands with a width of 20 μm with a shift of the analyzed area of 6.6 μm. The microspectrometric measurement (Figure 5) reveals that the oxidation photoproducts appear only in the first 40 μm and that most of the photooxidation occurs in the first 10 μm.

3. Surface Measurements. A determination of the profile of the light absorption was made on the basis of the extinction coefficient of polystyrene at 253.7 nm. This profile is reported in Figure 5 and shows that 98% of the incident light is absorbed in the first 10 μm. Comparison of both curves shows that diffusion of radicals or products can occur through the first layers and extend the width of the zone where photooxidation occurs. However, it remains true that the photooxidation at 253.7 nm is a surface reaction. The detection and identification of reaction products reported previously have been made by transmission spectroscopy techniques. As reactions occur in the first 10–20 μm, the sensitivity of such methods is reduced since the nondegraded part of the polymer is analyzed at the same time. For that reason, surface analysis using attenuated total reflection (ATR) was carried out.

Figure 6 shows that the ATR spectrum of the photooxidation products in the carbonyl domain is similar to that observed on the transmittance spectra. This confirms that the reactions occur mainly at the surface of the film (a 1.3-μm depth of penetration was determined in this region). Moreover, the intensity of the band centered around 1710–1725 cm^{-1} is very important in comparison to the intensity of the bands at 1583 and 1600 cm^{-1} of polystyrene. However, it must be pointed out that the spectra are quite noisy and that finally poor information was obtained from these spectra. This was especially true when chemical derivatization treatments were carried out on photooxidized samples, and no accurate information could be obtained from ATR spectra of so-treated samples.

Quantitative analysis of the oxidation of the surface layers can be obtained from the evolution of the spectra

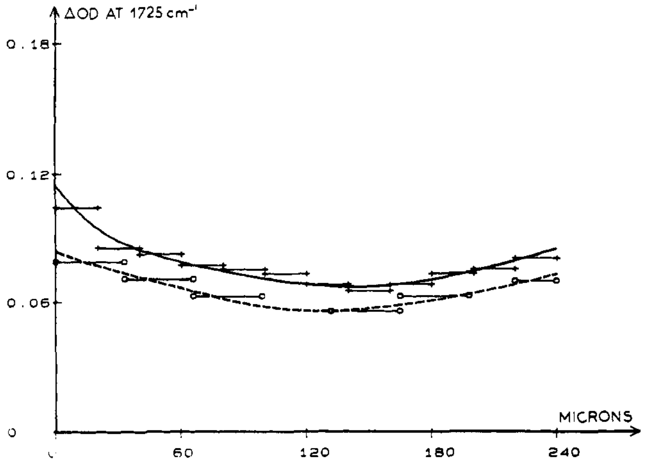


Figure 4. Concentration profile of a polystyrene film (thickness 240 μm) photooxidized at λ ≥ 300 nm and 60 °C: (- - -) 177 h; (—) 199 h.

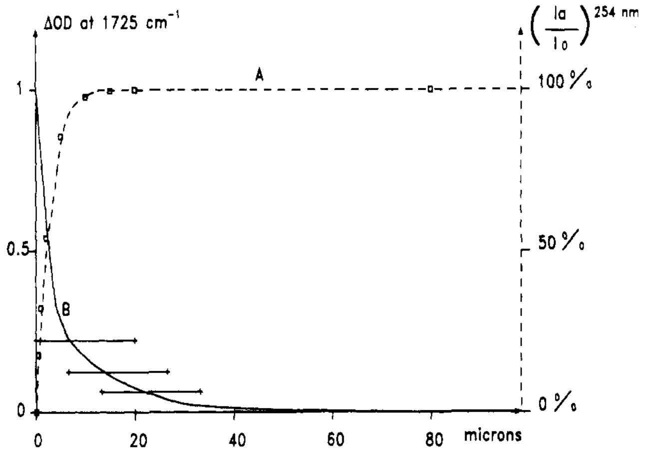


Figure 5. (A) Variation of the fraction of absorbed light intensity for polystyrene at λ = 253.7 nm versus film thickness. (B) Concentration profile of a polystyrene film (thickness 100 μm) photooxidized at λ = 253.7 nm at 30 °C for 292 h.

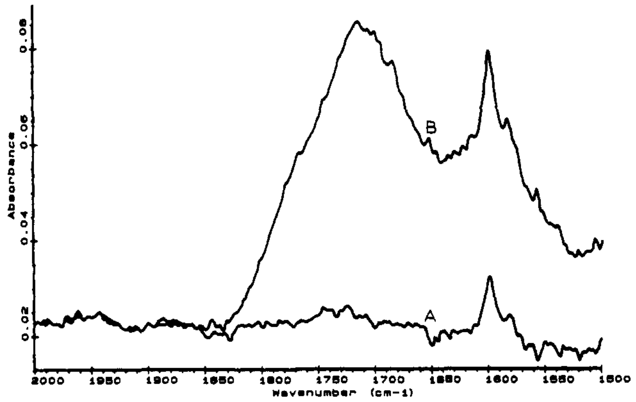


Figure 6. ATR analysis (KRS-5, 45° crystal, 200 scans) of a polystyrene film photooxidized for (A) 0 and (B) 280 h (λ = 253.7 nm, 30 °C).

of thin samples (7-μm thickness) exposed to short-wavelength irradiation. Analysis of their IR spectra was carried out by the transmission technique. Figure 7 shows the evolution of the spectra in the carbonyl and hydroxyl regions. The noise to signal ratio of these spectra is very low and accurate information can be obtained. That information confirms the above findings collected on thick samples.

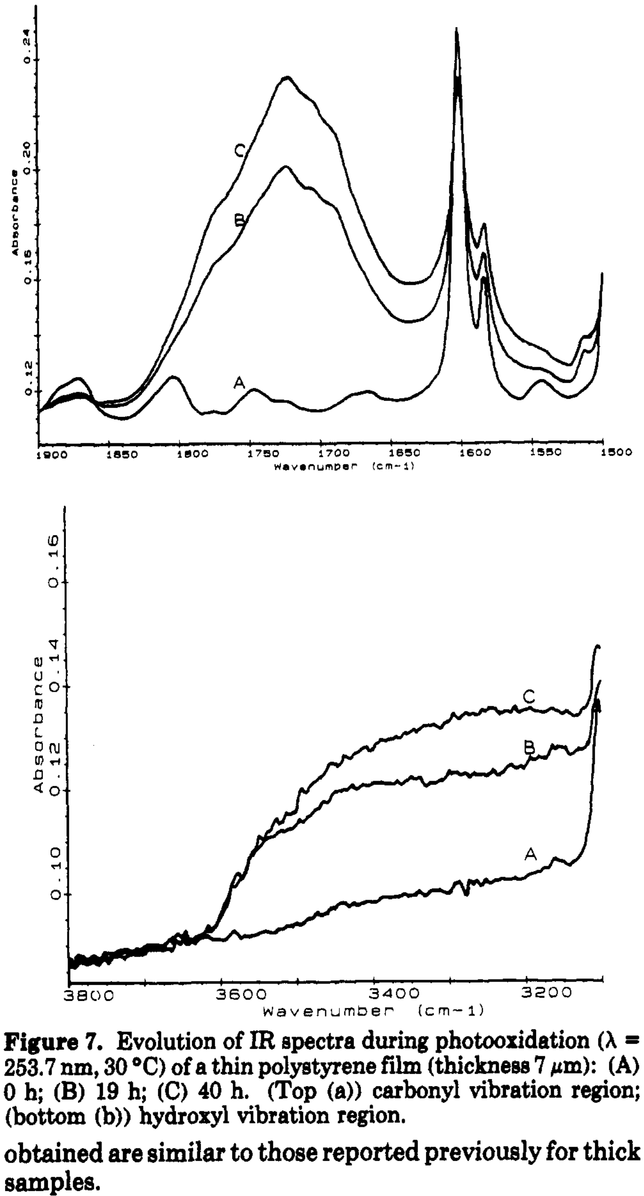


Figure 7. Evolution of IR spectra during photooxidation (λ = 253.7 nm, 30 °C) of a thin polystyrene film (thickness 7 μm): (A) 0 h; (B) 19 h; (C) 40 h. (Top (a)) carbonyl vibration region; (bottom (b)) hydroxyl vibration region.

Chemical derivatization reactions using SF_4 or NH_3 were also carried out on these thin films. The results that were obtained are similar to those reported previously for thick samples.

Comparison of the peak height ratio of the aromatic C–H stretch (3029 cm^{-1}) to the aliphatic C–H stretch (2923 cm^{-1}) band showed that no noticeable change was detected for irradiation of the 7-μm-thick film. In contrast, a marked decrease in the aromatic content was observed in the ATR spectra of the former sample.

Discussion

The results of the identifications of the oxidation photoproducts reported in the previous paper are sumarized in Table I. The following comments may be made:

Irradiation of polystyrene at short (λ = 253.7 nm) or long (λ ≥ 300 nm) wavelengths will cause the formation of macroradicals by abstraction of hydrogen on the polymeric backbone. It is not the aim of this paper to discuss the initial steps of the photolysis/photooxidation of polystyrene. It is generally agreed that photolabile structures containing oxygen are involved in the initial stages of photooxidation at long wavelengths and that the radicals obtained from the photolysis of these structures act as initiators of the oxidative phase of the degradation. This view permits one to explain the degradation of polymers such as polystyrene which contain no chromophores having an absorption in the long-wavelength region. The initial steps of the photooxidation of PS exposed to long-wavelength radiation have been discussed by Weir and Whitting.[4]

In principle, two types of macroradicals may be formed. Tertiary polystyryl radicals, $-CH_2\dot{C}(Ph)CH_2-$, have been identified by ESR measurements.[5,6] The lifetime of polystyryl radicals at room temperature in a vacuum has been found to be rather long.[7] Secondary radicals, $-CH(Ph)\dot{C}HCH(Ph)-$, could be formed, but no experimental observation supports this hypothesis.[8]

Once formed, the polystyryl radicals then add to oxygen to form peroxy radicals, $-CH_2C(Ph)(OO^\bullet)CH_2-$, which have also been identified by ESR spectroscopy.[7]

Abstraction of hydrogen on the macromolecular chain by the peroxy radical so-formed leads to a hydroperoxyl group, $-CH_2C(Ph)(OOH)CH_2-$. These groups are detected by the IR absorption at 3450 cm^{-1}. This wavenumber is approximately the maximum of a broad band corresponding to intermolecularly bonded OH groups including both hydroperoxyl and hydroxyl groups. The contribution of hydroperoxides to the whole absorption may be deduced from the photolysis of samples prephotooxidized at $\lambda \geq 300$ nm (the broad band at 3450 cm^{-1} was observed to decrease).

On the basis of previous assignment,[9] it is frequently agreed to assign the absorption band at 3540 cm^{-1} to free hydroperoxides.[10,11] However, the results of a photolysis of photooxidized samples show that the photolysis of hydroperoxyl groups leads to an increase of the absorption band at 3540 cm^{-1}. This result is not compatible with an attribution of the maximum at 3540 cm^{-1} to photolabile products such as hydroperoxides. This evolution is easily observed for long-wavelength irradiation since the band at 3540 cm^{-1} is more intense under these conditions of irradiation than under conditions of short-wavelength irradiation. Moreover, recent experiments[12] using treatments by sulfur dioxide on photooxidized films have shown that the band at 3540 cm^{-1} remained unchanged after the SO_2 treatment (SO_2 has been shown previously to efficiently reduce hydroperoxides[13]).

The decomposition of hydroperoxyl groups either by photolysis or by thermolysis leads to the formation of an alkoxy macroradical, $-CH_2C(Ph)(O^\bullet)CH_2-$, that may react in one of several ways:

(i) By abstraction of a hydrogen atom to the polymeric backbone, hydroxyl groups $-CH_2C(Ph)(OH)CH_2-$ are formed. These hydroxyl groups are detected by their IR absorption at 3540 (free OH) and 3450 cm^{-1} (intermolecularly bonded OH).[1]

(ii) β-Scission of the macroalkoxy radical may occur. Two types of scission are possible: (1) scission of the C–Ph bond and (2) scission of the $C-CH_2$ bond.

Scission 1 leads to a chain ketone $-CH_2C(O)CH_2-$ that corresponds to the maximum at 1725 cm^{-1}.[1,17] Scission 1 leads also to a benzyl radical that is the precursor of benzene, whose formation has been reported earlier.[14]

Scission 2 leads to an acetophenone type structure $-CH_2C(O)Ph$. This structure is responsible for the maximum at 1690 cm^{-1} (our previous observations have shown that this product did not react with SF_4 or NH_3). The formation of such ketonic end groups in photooxidized polystyrene has been reported.[15–17]

Scission 2 leads also to a macroradical $^\bullet CH_2CH(Ph)CH_2-$. This radical may react by one of two possible routes: either direct addition of oxygen or isomerization to yield a stable tertiary radical $CH_3\dot{C}(Ph)CH_2-$.

Similar isomerizations are reported to occur in polypropylene photooxidation: $^\bullet CH_2CH(CH_3)CH_2- \rightarrow CH_3\dot{C}(CH_3)CH_2-$. These isomerizations are responsible for the formation of acetone by further oxidation of the tertiary radical so obtained.[20]

Oxidation of the primary radical $-CH_2CH(Ph)CH_2^\bullet$ would lead to a carboxylic acid with the structure $-CH(Ph)COOH$. Such an acid is not detected among the oxidation products (no evidence of formation of $-CH(Ph)COF$ by SF_4 treatment), and this way has to be ruled out.

By oxidation of the tertiary radical $CH_3\dot{C}(Ph)CH_2-$ an alkoxy radical $CH_3C(Ph)(O^\bullet)CH_2-$ is obtained. The reactivity of this radical is very similar to the reactivity of the radical $-CH_2C(Ph)(O^\bullet)CH_2-$. The only difference is that the β-scission of this radical gives end-chain ketones [$CH_3C(O)CH_2-$ (1725 cm^{-1})], acetophenone groups $PhC(O)CH_2-$ (1690 cm^{-1}) and acetophenone as already described.[1] Indeed acetophenone has been detected by HPLC analysis of the extract by methanol. This confirms previous results which had shown that small quantities of acetophenone were formed.[17] The maximum at 1690 cm^{-1} corresponds then to acetophenone end groups and acetophenone.

Photochemical oxidation of the end-chain ketone $CH_3C(O)CH_2-$ involving Norrish type I reaction leads to a carboxylic acid $HOOCCH_2-$ (1710/1753 cm^{-1}) that can be obtained also by photochemical oxidation of the chain ketone $-CH_2C(O)CH_2-$ and leads also to acetic and formic acids (1710 cm^{-1}).

Acetophenone end groups $PhC(O)CH_2-$ formed by β-scission of the macroalkoxyradical $-C(Ph)(O^\bullet)CH_2-$ react photochemically following two different routes: scission of the $C-CH_2$ bond gives a radical $Ph\dot{C}(O)$ that can abstract a hydrogen atom or add to oxygen. The first reaction leads to benzaldehyde (1704 cm^{-1}), which is detected by HPLC analysis[1] and has been detected in the gas phase.[17] Benzaldehyde is oxidized in benzoic acid,[19] which presents absorptions at 1698 and 1732 cm^{-1}. Oxidation of the radical $Ph\dot{C}(O)$ gives the same reaction. The scission of the C–Ph bond leads to radicals $-CH_2\dot{C}(O)$. Oxidation of this radical may be the precursor of the carboxylic acid $-CH_2COOH$, whose formation has been reported.

Oxidation and/or reactions involving the radical $Ph\dot{C}(O)$ lead also to the formation of benzoic anhydride, $PhC(O)OC(O)Ph$. Benzoic anhydride is detected by IR absorptions at 1725 and 1785 cm^{-1} and characterized from reactions with NH_3 and MeOH. No detailed mechanism can be proposed since several plausible routes exist.

The formation of a molecular product with the structure of dibenzoylmethane, $C(O)(Ph)CH_2C(O)(Ph)$, has also been shown to occur. The formation of this product confirms the idea that oxidation of many polymers involves a zip oxidation of neighboring carbon atoms as suggested for polypropylene. The propagation of the oxidation reaction may result from attack on the tertiary carbons by hydroxyl radicals, $HO^\bullet$, obtained by decomposition of hydroperoxides. A cage effect favors then the reaction on the neighboring tertiary carbon atom:

$$-CH_2C(Ph)(OOH)CH_2CH(Ph)- \xrightarrow{h\nu/\Delta} -CH_2C(Ph)(O^\bullet)CH_2\dot{C}(Ph)- + H_2O$$

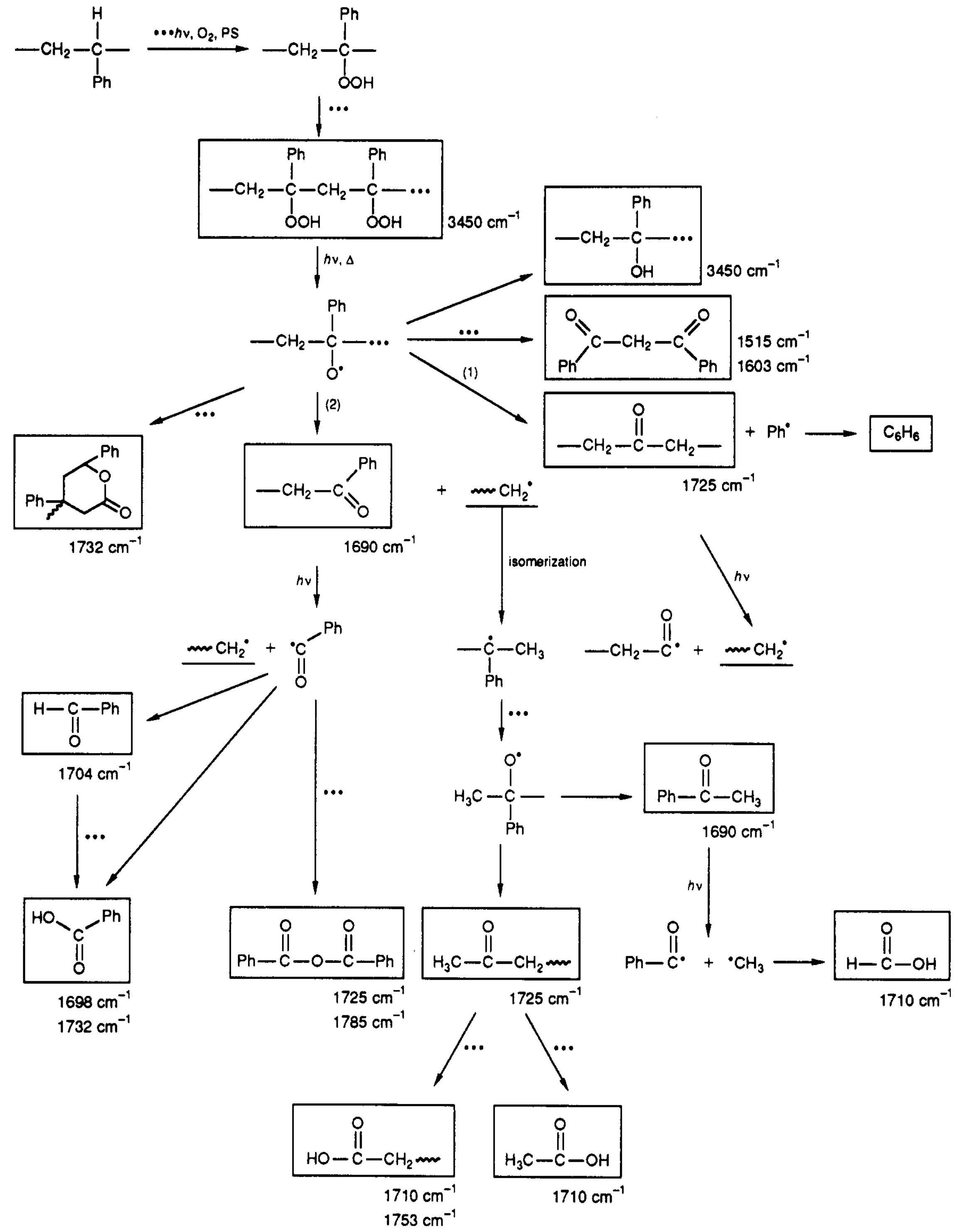
This radical evolves by β-scission and oxidation. A new alkoxy radical may then be obtained:

$$-CH_2C(Ph)(O^\bullet)CH_2\dot{C}(Ph)- \dashrightarrow PhC(O)CH_2C(Ph)(O^\bullet)-$$

By β-scission of this radical dibenzoylmethane is then obtained.

This discussion leads to a proposed general mechanism that accounts for the photochemical oxidation of polystyrene. This mechanism is presented in Scheme I.

Scheme I
Mechanism of Polystyrene Photooxidation



Except for the initial stages of initiation as discussed above, this mechanism can describe the short- and long-wavelength photooxidations. As shown earlier, the same photoproducts are observed under both conditions, but it remains true that their stationary concentrations are different, and then some differences are observed concerning the shape of the IR oxidation bands.

In the hydroxyl domain, the band at 3540 cm^{-1} of free hydroxyl groups $-CH_2C(Ph)(OH)CH_2C(Ph)H-$ is quite intense for irradiation at long wavelengths at 60 °C. In contrast, this band is hard to observe for irradiation at short wavelength, which explains probably the difficulties in assigning this maximum that have been underlined above. We have shown that the photoproducts of short-wavelength oxidation are formed in very superficial layers. These surface layers are then thoroughly oxidized, and the different photoproducts reach very high local concentrations. Their observation by IR spectroscopy reveals a weak contribution of free groups. In contrast, long-wavelength irradiation leads to a homogeneous distribution of the photoproducts through the oxidized matrix. Their local concentration is quite low and free hydroxyl groups can be observed.

Analysis of the surface layers (approximately 2 μm thick) of samples photooxidized at 254 nm confirms that the oxidation photoproducts present a heterogeneous distribution even in the first 15 μm where the short-wavelength

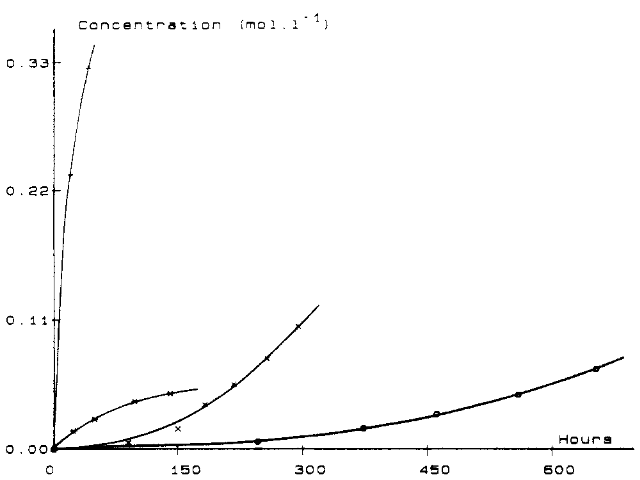


Figure 8. Acetophenone group concentration vs irradiation time of a polystyrene photooxidized at λ ≥ 300 nm and T = 60 °C (×), λ ≥ 300 nm and T = 30 °C (○), and λ = 253.7 nm and T = 30 °C [(+) film thickness 7 μm; (*) film thickness 75 μm].

photooxidation of the low molecular weight photoproducts near the surface.

This heterogeneous distribution of the oxidation photoproducts is also responsible for the evolution of the "aromatic to aliphatic absorption" ratio that is observed to decrease with the thickness analyzed. Such a behavior has already been observed by Lucas and Porter[11] and attributed to an oxidation that would involve an opening of the phenyl rings, confirming in this manner the reaction mechanism proposed by Lucki and Ranby.[9,18] However, as pointed out above, we have shown that the aromatic low molecular weight products formed may diffuse out of the polymer sample, resulting in a concentration gradient. This behavior is responsible for the evolution of the ratio of aromatic to aliphatic C–H stretching intensities, and no direct evidence is then given for a reaction on the phenyl rings.

In the carbonyl domain, the differences between the shape of the oxidation bands observed after irradiation in the SEPAP 12-24 and the SEPAP 253.7 units have to be attributed to a temperature effect. This is proved by the result of an irradiation in the SEPAP 14–24 unit at 30 °C, since the oxidation band is rather similar to the one obtained in the SEPAP 253.7 at the same temperature. Irradiation carried out at 60 °C leads to an oxidation band in which no contribution of the formic and acetic acids is observed. Such an evolution can be reproduced by submitting a sample photooxidized at 30 °C to a thermolysis at a temperature above 100 °C: the diffusion of acetic and formic acids out of the polymer films gives a carbonyl band very similar to the band observed for irradiations carried out at 60 °C. Since the boiling point of both acids is more than 100 °C, it may be assumed that under conditions of an irradiation at 60 °C, it is the precursor of these products, actually acetophenone (bp = 56 °C), that evaporates out of the sample.

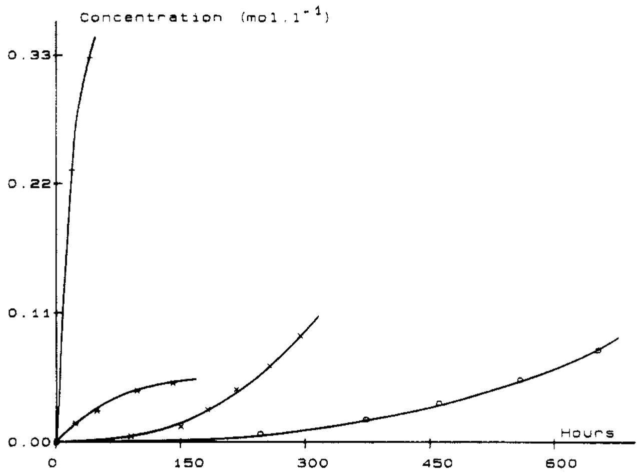


Figure 9. Carboxylic acid concentration vs irradiation time of a polystyrene photooxidized at λ ≥ 300 nm and T = 60 °C (×), λ ≥ 300 nm and T = 30 °C (○), and λ = 253.7 nm and T = 30 °C [(+) film thickness 7 μm; (*) film thickness 75 μm].

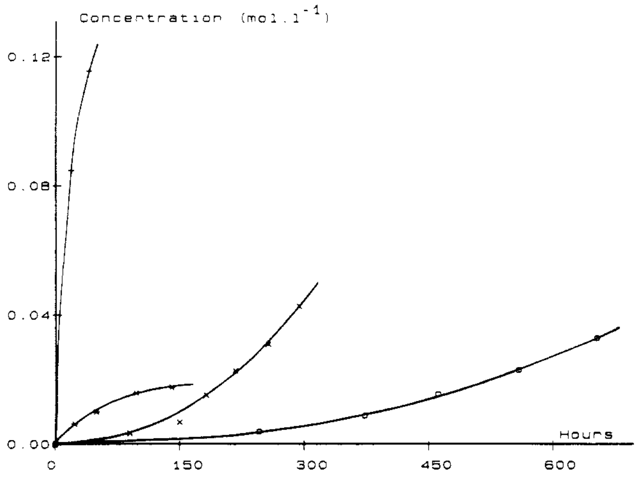


Figure 10. Benzoic anhydride concentration vs irradiation time of a polystyrene photooxidized at λ ≥ 300 nm and T = 60 °C (×), λ ≥ 300 nm and T = 30 °C (○), and λ = 253.7 nm and T = 30 °C [(+) film thickness 7 μm; (*) film thickness 75 μm].

From the spectra presented in Figures 1 and 7 of paper 1 and Figures 2 and 7 of the present paper, it is possible to plot the accumulation of some photoproducts as a function of irradiation time. Using reasonable values for the extinction coefficients derived from model compounds ($\epsilon^{1690\text{cm}^{-1}}_{\text{acetophenone}} = 446$ M^{-1} cm^{-1}, $\epsilon^{1710\text{cm}^{-1}}_{\text{carboxylic acid}} = 500$ M^{-1} cm^{-1}, $\epsilon^{1785\text{cm}^{-1}}_{\text{benzoic anhydride}} = 745$ M^{-1} cm^{-1}), the evolution of the concentrations of acetophenone groups at 1690 cm^{-1}, carboxylic acids at 1710 cm^{-1}, and benzoic anhydride at 1785 cm^{-1}, can be presented (Figures 8–10). From these figures, the following comments may made:

The mean concentrations measured for short-wavelength irradiation depend on the thickness of the samples and are higher for thin samples (7 μm). This occurs because the absorption of light is very superficial. The major part of the thick sample (75 μm) remains unoxidized on irradiation at 253.7 nm.

The quantum yield of formation of acetophenone groups (1690 cm^{-1}) can be obtained from the curve (+) on Figure 8. The value of 5×10^{-4} that is determined is in a good accordance with the results published by Geuskens et al.[17]

The concentration ratios of acetophenone groups and benzoic anhydride are not dependent on the conditions of irradiation and remain nearly constant when the wavelength or the temperature changes.

The concentration ratios of the carboxylic acids at 1710 cm^{-1} and either benzoic anhydride or acetophenone groups remain nearly constant for short-wavelength irradiation and long-wavelength irradiation at "low" temperature (30 °C) but, in contrast, decrease for irradiations at "high" temperature (60 °C).

Conclusion

One of the most noticeable points of the photochemical oxidation of polystyrene is that many photoproducts formed are molecular compounds. Most of them have been identified: benzaldehyde, benzoic acid, acetophenone, formic acid, acetic acid, benzoic anhydride, dibenzoylmethane, and benzene. Depending on the conditions of irradiation, some of these products may diffuse out of the photooxidized samples, and IR analysis reveals apparent differences of stoichiometries that may be confused with wavelength effects.

References and Notes

(1) Mailhot, B.; Gardette, J. L. *Macromolecules*, preceding paper in this issue.
(2) Lemaire, J.; Arnaud, R.; Gardette, J. L. *Rev. Gen. Caoutch. Plast.* **1981**, *613*, 87.
(3) Jouan, X.; Gardette, J. L. *Polym. Commun.* **1987**, *28*, 329.
(4) Weir, N. A.; Whiting, K. *Eur. Polym. J.* **1989**, *3*, 291.
(5) Cozzens, R. F.; Moniz, W. B. *J. Chem. Phys.* **1968**, *48*, 581.
(6) David, C.; Piret, W.; Sekiguchi, M.; Geuskens, G. *Makromol. Chem.* **1978**, *179*, 181.
(7) Toriakai, A.; Takeuchi, T.; Fueki, K. *Polym. Photochem.* **1983**, *3*, 307.
(8) Weir, N. A. *Developments in Polymer Degradation*; Grassie, N., Ed.; Applied Science: London, 1982; Vol. 4, p 143.
(9) Lucki, J.; Ranby, B. *Polym. Degrad. Stab.* **1979**, *1*, 1.
(10) Dickens, B.; Marchal, J. *Polym. Degrad. Stab.* **1984**, *6*, 211.
(11) Lucas, P. C.; Porter, R. S. *Polym. Degrad. Stab.* **1988**, *22*, 175.
(12) Mailhot, B.; Gardette, J. L., unpublished results.
(13) Gardette, J. L.; Lemaire, J. *Polym. Photochem.* **1986**, *7*, 409.
(14) Khalil, K.; Michaille, S.; Lemaire, J. *Makromol. Chem.* **1987**, *188*, 1743.
(15) Beachell, H. C.; Smiley, L. H. *J. Polym. Sci.* **1967**, *5*, 1635.
(16) Kato, K. *J. Appl. Polym. Sci.* **1971**, *15*, 2115.
(17) Geuskens, G.; Baeyens-Volant, D.; Delaunois, G.; Lu-Vinh, Q.; Piret, W.; David, C. *Eur. Polym. J.* **1978**, *14*, 291.
(18) Rabek, J. F.; Ranby, B. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *14*, 273.
(19) March, J. *Advanced Organic Chemistry*; McGraw-Hill Kogakusha: Tokyo, 1977.
(20) Lacoste, J., personal communication.

Registry No. PS, 9003-53-6.