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Influence of the chemical structure of polycarbonates on the contribution of crosslinking and chain scissions to the photothermal ageing

A. Rivaton *, B. Mailhot, J. Soulestin, H. Varghese, J.-L. Gardette

Laboratoire de Photochimie, Moléculaire et Macromoléculaire, UMR CNRS 6505, Université Blaise Pascal (Clermont-Ferrand), F-63177 Aubière Cedex, France

Abstract

The relative importance of crosslinking and chain scissions reactions involved in the photothermal ageing of polycarbonates is shown to depend on the chemical structure of the polymer. The orientation of these reactions is linked to the modifications of the chemical structure resulting from photolysis, photooxidation and thermooxidation. In this paper, the effects of crosslinking and chain scission of tetramethyl bisphenol-A polycarbonate (TMPC) are determined by size exclusion chromatography (SEC) and gel fraction measurements. These evolutions are correlated to the modifications of the chemical structure observed by FTIR spectroscopy.

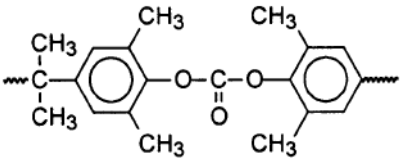
The presence of the four *ortho*-methyl substituants on the aromatic rings accounts for the difference in the photothermal ageing of TMPC compared to bisphenol-A polycarbonate (PC). Tetramethyl substitution inhibits photo-Fries rearrangements in TMPC, but in contrast these methyl groups involve crosslinks under irradiation and are the source of a higher oxidizability of TMPC compared to PC. A proposal for the various routes accounting for the crosslinking and the formation of the oxidation products in TMPC is reported in this paper.

1. Introduction

In addition to degradation of the aspect which is particularly important in the case of bisphenol-A polycarbonate (PC) the understanding of the crosslinking and chain scission reactions is of prime importance for the prevision of the behaviour of the polymer in term of mechanical properties.

PC exhibits excellent physical properties such as transparency and rigidity. However, exposure of PC to sunlight leads to a significant loss of these properties. In particular, the photo-yellowing of PC limits the use of this material in case of outdoor applications [1–3].

Photo-Fries rearrangements of the carbonate moieties in *ortho* position has been shown to be responsible for the photo-yellowing due to a non-oxidative discolouration route of PC [4]. In order to prevent the formation of the photo-Fries products, the chemical structure of PC has been modified. Tetramethyl bisphenol-A polycarbonate (TMPC), in which the four *ortho* positions of the phenyl rings of PC are substituted by methyl groups, has been synthesised:



Scheme 1 : TMPC structure

In a previous paper, the photooxidation and the thermooxidation of TMPC have been described [5]. The presence of *ortho*-methyl substituants was shown to account for the difference in the photothermal ageing of TMPC and PC.

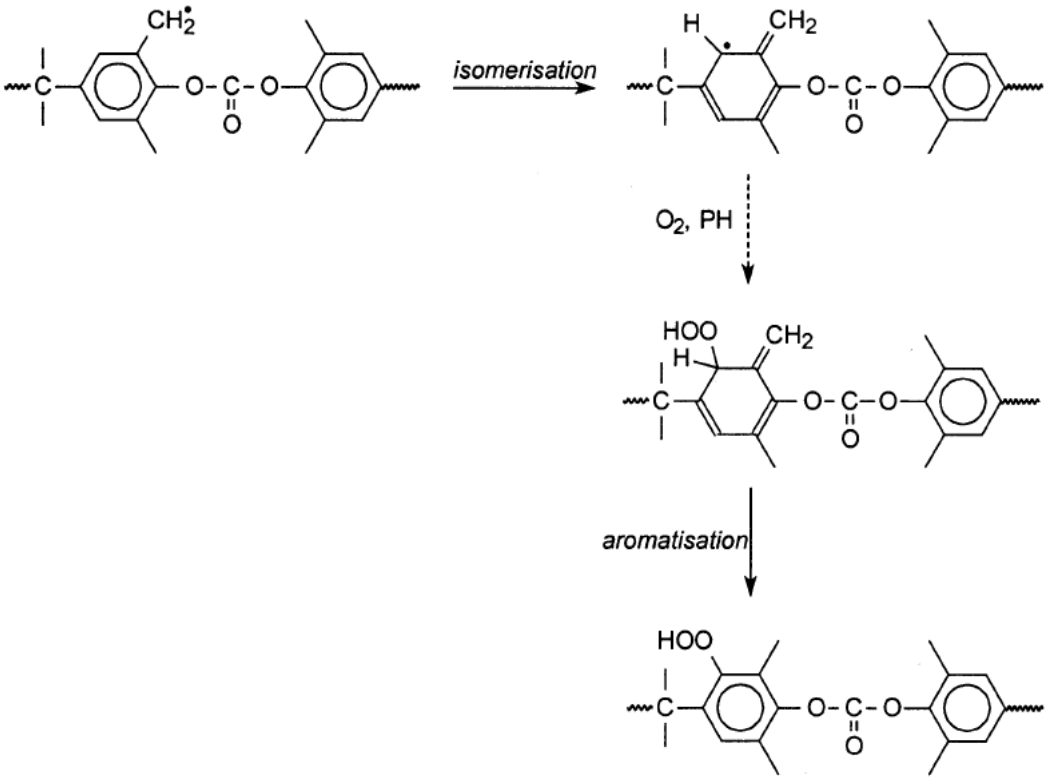
It was observed that, unlike PC, TMPC films become insoluble in $CHCl_3$ after a short exposure. However, such an observation was not connected to the evolution of the chemical structure of the polymer.

o-CH_3 substitution inhibits photo-Fries rearrangements, but these methyl groups are quite more oxidisable than the one of the isopropylidene moieties. Indeed it has been shown that a photo-induced oxidation of the *o*-CH_3 substituants is responsible for the main route of oxidation of TMPC. To account for such an oxidation pathway, the following mechanistic schemes have been proposed [5]:

Abstraction of hydrogen atom from *o*-CH_3 substituants by $R^{\bullet}$ (radicals arising from the photolysis of chromophoric structures) leads to the formation of primary benzyl radicals:

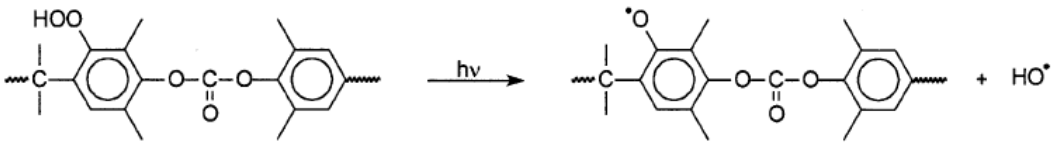
Scheme 2 : Hydrogen abstraction from o-CH_3 substituants

Once formed, the primary benzyl radicals rearrange to form more stable secondary radicals, which are readily oxidised and lead to aromatic hydroperoxides. The isomerisation giving the secondary radical has been proposed to explain the relatively high concentration of hydroperoxides having a notable stability at high temperature, property incompatible with primary hydroperoxides (PH represents the polymer):



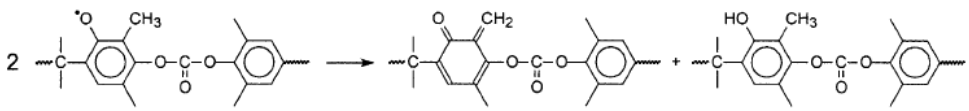
Scheme 3 : formation of aromatic hydroperoxides

The homolysis of the O–O bond of the hydroperoxides, which can occur on irradiation or at high temperature, leads to the formation of alkoxy radicals:



Scheme 4 : homolysis of the hydroperoxides

The oxidation of these radicals is responsible for the formation of several hydroxylated and carbonylated compounds. These oxidation products have not been identified in the previous paper, except the one with an IR vibration band at 1655 cm^{-1} that has been tentatively attributed to the formation of a quinone-methide structure. The following disproportionation reaction has been proposed:



Scheme 5 : formation of quinone-methide and phenolic structures

On the basis of the published data, one cannot consider the mechanism of the photo-ageing of TMPC as being established conclusively. Many steps remain unknown since the ratio crosslinking/chain scission was not evaluated and since most of the oxidation products have not been identified.

A better analysis of the modification of the chemical structure of the polymer is now permitted by the improvement of the analytical techniques, such as size exclusion chromatography (SEC), gel fraction measurements as well as the association of chemical derivatisation reactions with infrared spectroscopic analysis.

Since the comparison of the behaviours in thermooxidation and in photooxidation can be very helpful to elucidate the mechanisms, the thermooxidation of TMPC has also been studied. Therefore, the modification of the chemical structure of TMPC throughout irradiation at long wavelengths ($\lambda > 300$ nm) or after thermooxidation at 170 °C is attempted.

Using these analytical techniques, it is now possible to propose a much more detailed mechanism of photothermal ageing of TMPC with the aim of understanding the influence of the tetramethyl substitution on the occurrence of the various reactions.

2. Experimental

Non-stabilised PC and TMPC granulates were supplied by Aldrich and Bayer (Germany) respectively. Thin films (15–25 μm) submitted to irradiation were obtained by evaporation of polymer solutions in $CHCl_3$. Thick films (100–200 μm) submitted to thermooxidation were obtained by compression moulding between PTFE-coated glass cloth at 200 bars and 280 °C: PC for 90 s and TMPC for 30 s.

Irradiations were carried out in a SEPAP 12.24 unit at a temperature of 60 °C. This apparatus has been designed for studies of polymer photodegradation in artificial conditions corresponding to a medium acceleration of the ageing; this unit allows irradiation at long wavelengths ($\lambda > 300$ nm) [4]. Low temperature thermooxidation experiments were carried out in an aerated oven at 170 °C.

Average molecular weights (M_w) of polymeric samples were obtained by SEC. SEC was carried out on a Waters 600 Controller using Plgel 7.5 mm ID column and a Waters 2487 – Dual λ absorbance detector. The mobile phase was chloroform with a flow rate of 1 ml/min. The calibration was achieved using polystyrene standards.

As a complement, the crosslinking of PC and TMPC was studied by measuring the density of solutions in $CHCl_3$ of the soluble part of irradiated samples according to a technique described earlier [6].

The macromolecular hydroperoxides formed in the photooxidised samples were titrated using an iodometric method [7].

Irradiated films were exposed to reactive SF_4 (Fluka) and NH_3 (Ucar) gases at room temperature in all-Teflon reactors. Coupling the IR analysis with chemical derivatisation reactions allows an in situ identification of the carboxylic acids, esters, aldehydes and anhydrides groups [8,9].

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

IR spectra were recorded on a Nicolet 760 FTIR spectrophotometer (nominal resolution of 4 cm^{-1}, 32 scans summation). UV spectra were recorded on a Shimadzu UV-2101PC spectrophotometer equipped with an integrating sphere. The fluorescence spectra were obtained using a Jobin–Yvon JY3D spectrofluorimeter. Measurements of photoproducts profiles in irradiated films were performed on a Nicolet 760 equipped with a NICPLAN microscope (liquid nitrogen-cooled MCT detector, 128 scan summations) [10]. The irradiated films were pressed between two polypropylene plates and then sliced with a Reichert and Jung microtome. Slices with a thickness of ≈50 μm were obtained and then examined through the FTIR microscope. The spectra were recorded every 11 μm from the irradiated surface towards the core of the sample.

HPLC analysis of the low molecular weight photoproducts, extracted by immersion of the irradiated films in methanol, were performed on a Merck chromatograph equipped with a photodiode array detector. The column was a Hewlett Packard reverse-phase C18, 5 μm (250 × 4 mm). The mobile phase was a gradient acetonitrile (Fisons HPLC solvent)–water (acidified with 2/1000 H_3PO_4). The outflow was 1 ml/min.

3. Experimental results

3.1. Chemical changes in the solid polymer

3.1.1. Molecular weight changes upon irradiation

PC and TMPC films are soluble in $CHCl_3$ at room temperature. But after irradiation, in the presence and in the absence of oxygen, and after thermooxidation an insoluble part is produced. The amount of insoluble material formed throughout the degradation was measured by densimetry; results are reported in Fig. 1.

Crosslinking appears to be the major phenomenon occurring during the initial period of the irradiation of TMPC films. The amount of insoluble fraction increases faster when irradiation is carried out in the presence than in the absence of oxygen.

Microgel formation of the TMPC films occurs at lower extent in thermooxidation than in photooxidation. The photooxidation of PC involves a lower microgel formation compared to TMPC; for the same duration, no degradation of the PC thermooxidised matrix was measured.

The evolution of the molecular weight (M_w) of the soluble fraction in $CHCl_3$ at room temperature of degraded films was determined by SEC. Results are shown in Fig. 2.

The M_w of the soluble fraction of thermooxidised TMPC films and irradiated PC films gradually decreases. In contrast, the M_w of irradiated TMPC films increases rapidly under exposure and reaches a maximum value (125 000) within 5 h of irradiation in the presence of oxygen and 20 h in the absence of oxygen. Then an insoluble network is formed and M_w rapidly decreases, reaching a very low value: only oligomeric macromolecules remain soluble in $CHCl_3$.

The evolution of the M_w of TMPC is in good accordance with the chromatograms reported on Fig. 3. During the first 5 h of photooxidation the chromatogram of TMPC is broaden on the side of the higher molecular weight (Fig. 3a). After 10 h of photooxidation the chromatogram of TMPC is broaden, especially on the side of the lower molecular weights.

In contrast, the chromatogram of thermooxidised TMPC films is gradually shifted on the side of the lower molecular weights (Fig. 3b).

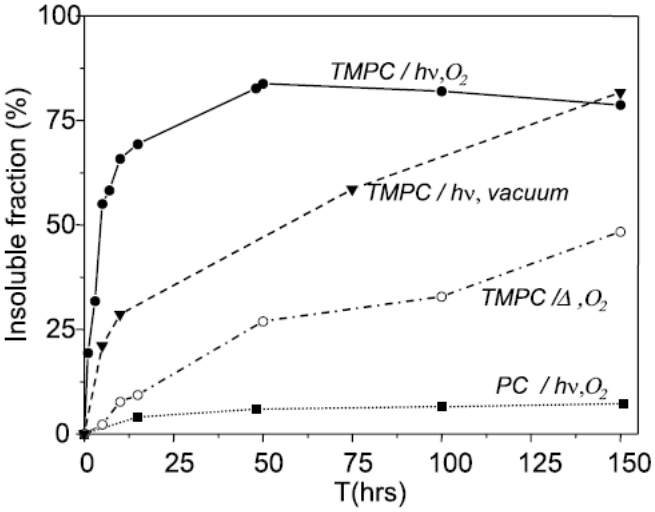


Fig. 1. Determination of the insoluble fraction of TMC and PC films as a function of photooxidation, photolysis and thermooxidation duration.

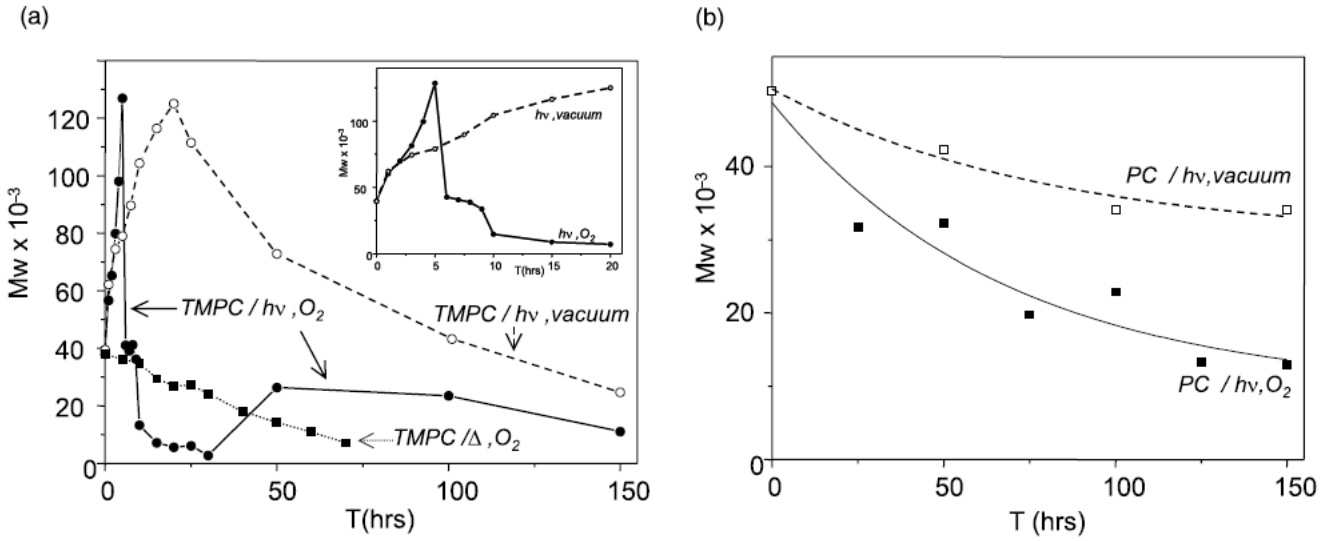


Fig. 2. Evolution of M_w of TMPC films irradiated at $\lambda > 300$ nm and thermooxidised at 170 °C (a) and of PC films irradiated at $\lambda > 300$ nm (b) as a function of degradation duration.

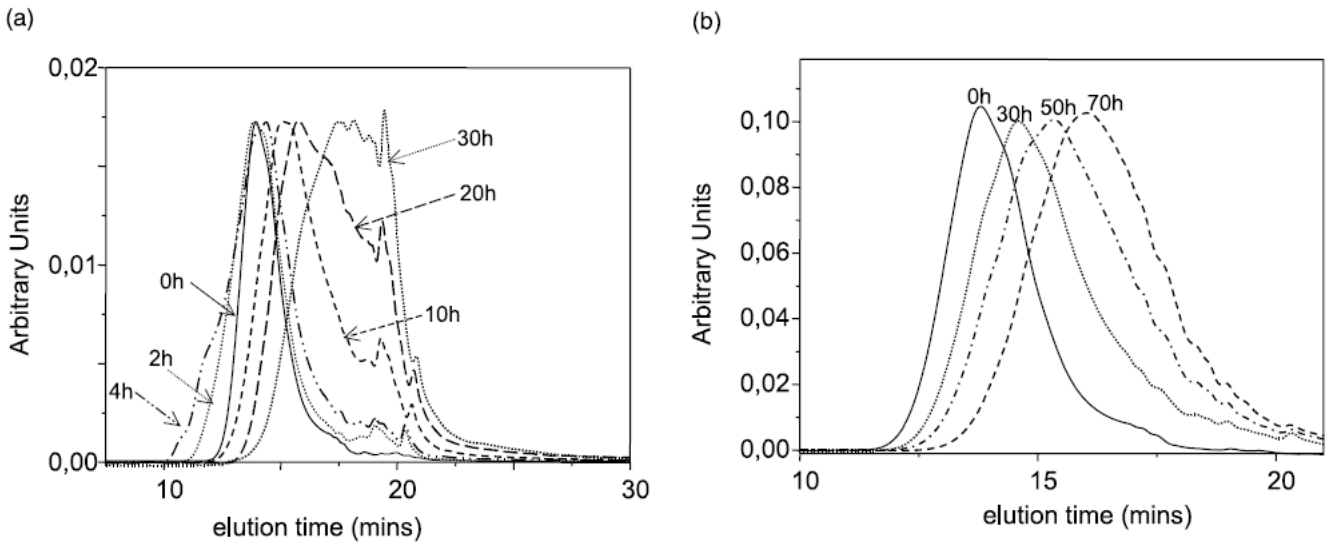


Fig. 3. Evolution of the GPC chromatograms of TMPC films throughout photooxidation at $\lambda > 300$ nm (a) and thermooxidation at 170 °C (b).

3.1.2. FTIR and UV–visible analysis

As expected, the IR spectra of the photo- and thermooxidised samples, recorded after various heating and exposure durations, show the same features as those previously reported [5]. A more acute information is obtained using a more performing FTIR apparatus. The subtraction of the initial spectrum before oxidation to the spectra recorded after several oxidation times allows the observation of several maxima that are formed in the carbonyl and hydroxyl broad bands.

In the carbonyl region (Fig. 4a), thermooxidation leads to the formation of maxima at 1704, 1696, 1655, 1613 and 1600 cm^{-1}.

At low extent of conversion (top left Fig. 4b), photooxidation leads to the formation of maxima at 1734, 1713, 1704, 1696, 1655, 1613 and 1600 cm^{-1}. As irradiation proceeds, the two maxima at 1704 and 1696 cm^{-1} cannot be observed on the IR spectra because the bands overlap with the pre-eminent IR band at 1713 cm^{-1} (Fig. 4b). This last absorption band was assigned to a product called P_{1713} [5].

In the hydroxyl region (Fig. 5), an increase of an absorption band is observed in thermooxidation with maxima or shoulders around 3550, 3500, 3450 and 3300 cm^{-1}. The relative intensities of the corresponding bands are different in thermo- and in photo-oxidative conditions. In photooxidation, a broad band centred around 3230 cm^{-1} becomes pre-eminent as irradiation proceeds.

In parallel, an important decrease in aromatic ν(C–H) at 3050 cm^{-1} and aliphatic ν(CH_2–H) at 2962 and 2872 cm^{-1} was monitored throughout irradiation.

In the UV–visible range, the photo- and thermo-oxidation of TMPC films generated an increase of absorption at wavelengths below 500 nm. On both spectra, a shoulder with a maximum around 340 nm was discerned.

As previously reported [5], the shape of the UV–visible and IR absorption bands formed in TMPC during photo- and thermo-oxidation is different from that observed in PC.

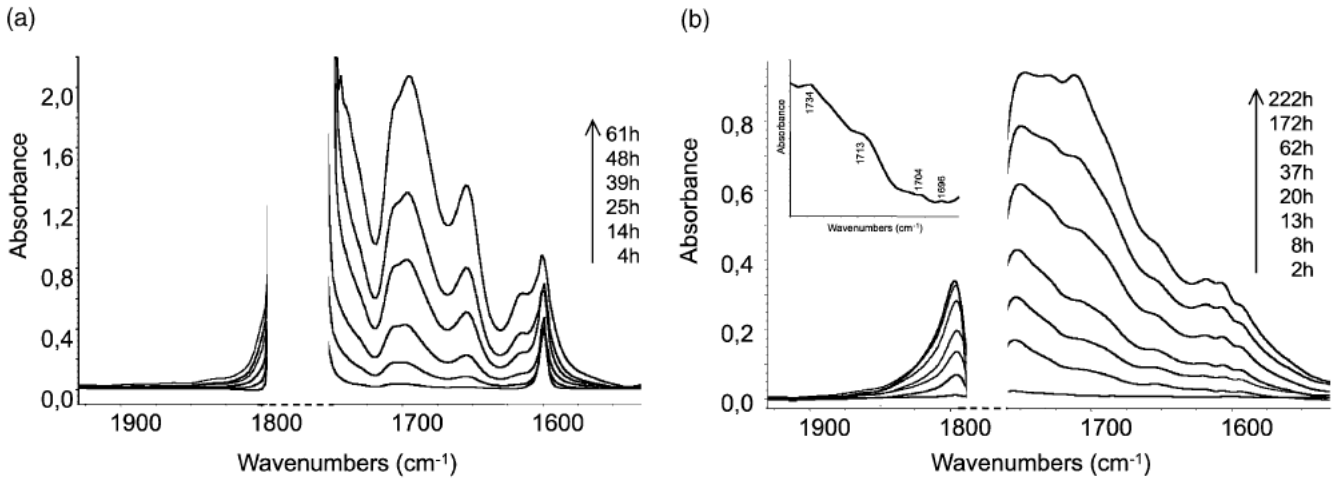


Fig. 4. FTIR spectra of a TMPC film in the carbonyl region (oxidised–non-oxidised sample) for various thermooxidation times at 170 °C (a) and for various photooxidation times at $\lambda > 300$ nm (b).

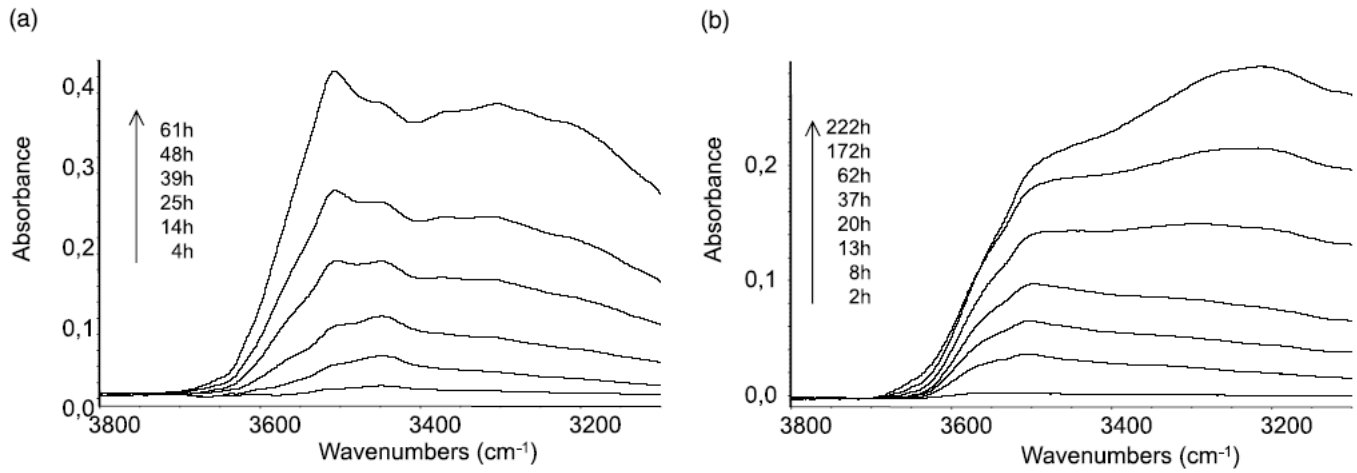


Fig. 5. FTIR spectra of a TMPC film in the hydroxyl region (oxidised–non-oxidised sample) for various thermooxidation times at 170 °C (a) and for various photooxidation times at $\lambda > 300$ nm (b).

3.1.3. Spatial distribution

A thick film (200 μm) of TMPC was irradiated for 100 h and the oxidation profile was determined by recording the spectra every 11 μm. The increase of absorbance in the hydroxyl range was measured and plotted (Fig. 6) as a function of the distance from the exposed face.

The oxidation photoproducts appear to be distributed heterogeneously in the TMPC sample as previously observed for PC [4]: only the first 40 μm of films are oxidised.

In contrast, no oxidation profile was observed in the films thermooxidised for the same duration. This result indicates that oxygen diffusion into the films does not control the rate of thermooxidation.

The fact that the products of the photooxidation are confined to the first 40 μm may be related to the light absorption of TMPC and PC films in the UV domain of the terrestrial solar radiation, which limits the photoreactions to the first microns.

Such an interpretation is confirmed by the analysis of TMPC films irradiated in the absence of oxygen. Vacuum photolysis of TMPC leads to the formation of phenolic structures observed in the hydroxyl region as a weak band peaking around 3530 cm^{-1} (Fig. 7).

In the UV–visible domain of films irradiated in the absence of oxygen, absorption was observed to increase below 500 nm without any defined observable maximum. Of course, no photo-Fries product was detected in the carbonyl region since rearrangements, that constitute the major route of PC photolysis, are forbidden in TMPC.

The photodegradation profile was observed to exhibit the same shape in the presence and in the absence of oxygen.

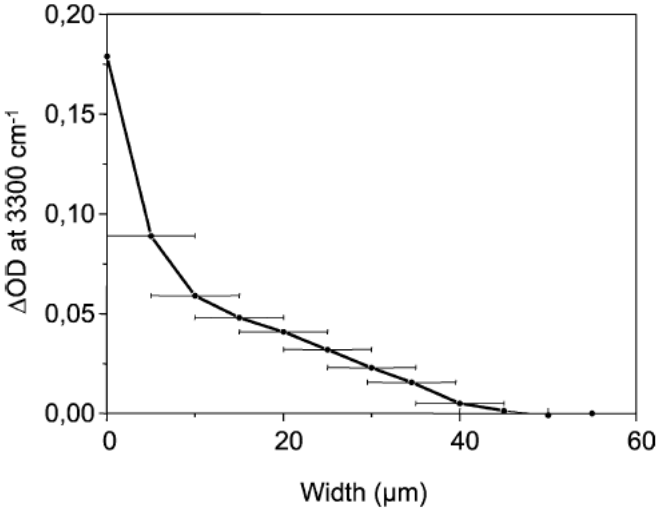


Fig. 6. Photooxidation profile measured by microFTIR spectroscopy of TMPC films (100 μm) irradiated 100 h at $\lambda > 300$ nm.

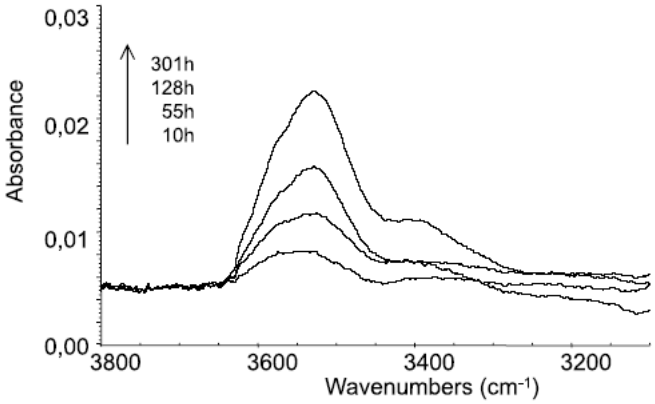


Fig. 7. FTIR spectra of TMPC film (b) in the hydroxyl region (irradiated–non-irradiated sample) for various photolysis times at $\lambda > 300$ nm in the absence of oxygen.

3.2. Detection of the low molecular weight species

3.2.1. Identification of the photoproducts by vacuum thermal treatment at 100 °C—Analysis of the volatile products

Thermolysis in vacuum at 100 °C of TMPC films pre-photooxidised for 50, 100 and 150 h was carried out.

Vacuum heating leads to the decrease of the carbonyl absorption between 1750 and 1690 cm^{-1} (Fig. 8), indicating a loss of some molecular compounds related to the disappearance of the band with a maximum at 1713 cm^{-1}.

The decrease of the absorption band at 1713 cm^{-1} allows the observation on the IR spectra of heated polymers of the residual bands at 1704 and 1696 cm^{-1}. The band at 1655 cm^{-1} remains unchanged in this treatment.

In the domain of hydroxyl vibrations, the decrease of the broad band located around 3230 cm^{-1} (range of associated OH groups of acids [11]) contributes for about 21% to the whole hydroxyl absorption. It is accompanied by the

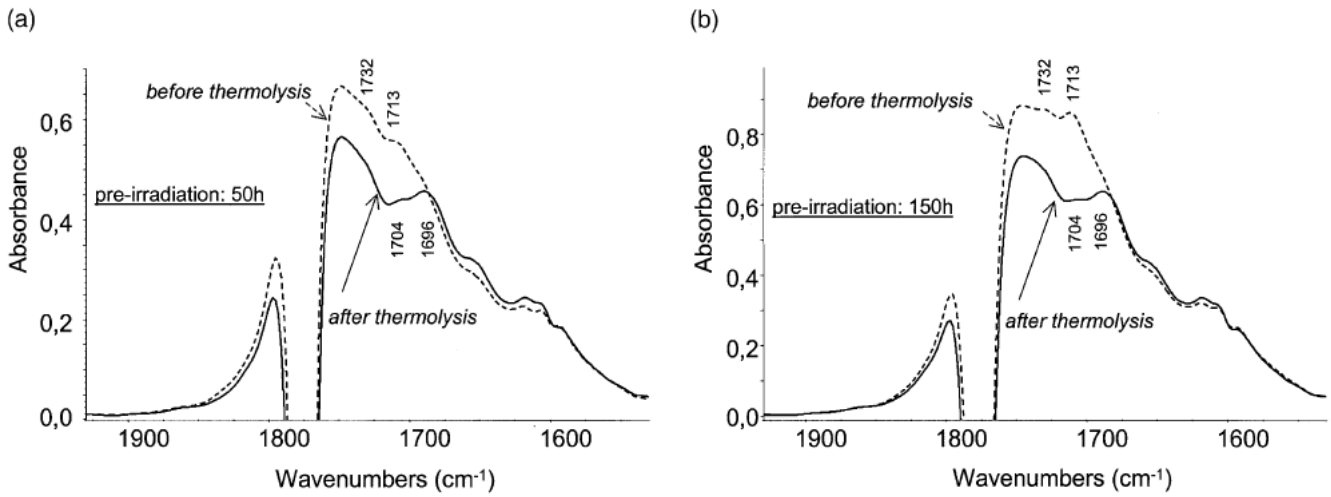


Fig. 8. Evolution of the IR spectra of a photooxidised TMPC film throughout post-thermal treatment at 100 °C. Duration of pre-irradiation: (a) 50 h, (b) 150 h.

Table 1
Decrease of absorbance at 1713 cm^{-1} produced by thermal treatment

Pre-irradiation duration (h)	PC	TMPC
50	0.00	−0.12
100	−0.02	−0.22
150	−0.06	−0.25

decrease of the absorbance at two weak shoulders around 3550 and 3430 cm^{-1} (free and intermolecularly bonded OH groups) that may be assigned to the homolysis of the hydroperoxydes.

Results of vacuum thermal treatments at 100 °C for 24 h of TMPC and PC films pre-photooxidised for various periods of time are reported on Table 1.

The analysis of Table 1 indicates that P_{1713} formed in both PC and TMPC can be thermally extracted and that the concentration of P_{1713} is higher in TMPC than in PC.

Infrared analysis of the gas phase was carried out. A large sheet of polymer was rolled in a Pyrex tube connected to a gas cell consisting of a long glass cylinder whose ends were KBr windows. The whole system was filled with oxygen and then sealed. Exposure of the tube containing the polymer was carried at $\lambda > 300$ nm and the gas was periodically analysed by IR spectroscopy throughout exposure in order to determine the composition of the gas phase.

The spectra show mainly absorption bands at 2361, 2338 and 671 cm^{-1} which indicate the formation of CO_2.

The formation of small amounts of water is observed in the hydroxyl region and traces of carbonyl groups are noticed at 1794 and 1772 cm^{-1} suggesting respectively the presence of gaseous formic and acetic acid in their dimer form. A confirmation of the nature of the products that migrate out of the sample in thermolysis has been obtained by mass spectroscopy analysis of PC, since formic and acetic acids have been unambiguously identified [4].

These identifications are in good agreement with the observations reported above on the evolution of the IR spectra of the so-treated films. The maxima observed to decrease at 1713 cm^{-1} and around 3230 cm^{-1} correspond to the vibrations of dimer and associated OH forms of acid groups.

As a conclusion, these experimental results indicate that P_{1713} may be assigned to low molecular weight aliphatic acid groups that can be lost by migration and evaporation at 100 °C from TMPC and PC films.

3.2.2. Identification of the photoproducts by methanol treatment—Analysis of the extractable photoproducts

Immersion in methanol of thermooxidised films has no effect on the IR spectra. On the contrary, immersion in methanol of photooxidised films leads to an important decrease of absorbance of the photooxidation products after few hours in the solvent (Fig. 9).

In the domain of carbonylated products absorption, methanol treatment has the same effect as vacuum heating (see Figs. 8 and 9). Methanol treatment provokes a decrease of the band with a maximum at 1713 cm^{-1} at a larger extent. The two bands at 1704 and 1696 cm^{-1} and the band at 1655 cm^{-1} remain unchanged in this treatment.

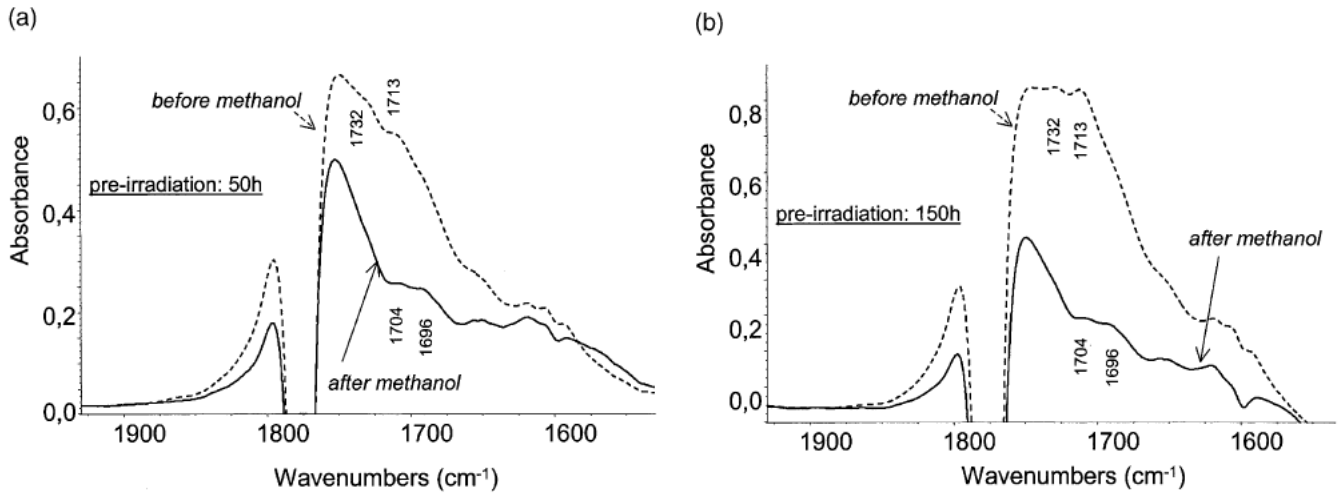


Fig. 9. Evolution of the IR spectra of a photooxidised TMPC film throughout post-immersion in methanol. Duration of pre-irradiation: (a) 50 h; (b) 150 h.

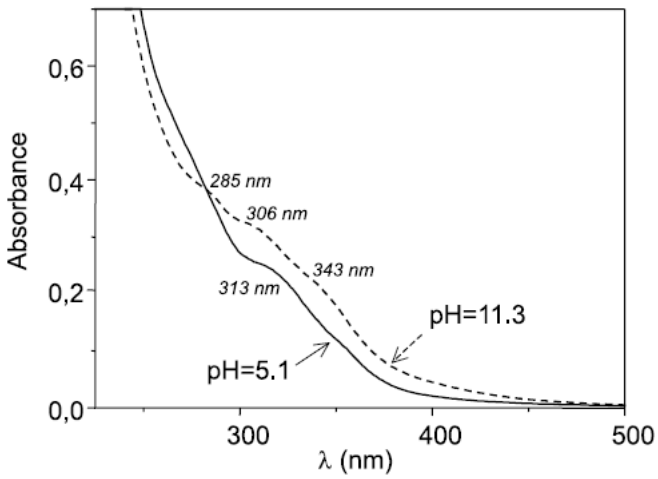


Fig. 10. UV–visible absorption spectra of the methanolic solution of the low molecular weight photoproducts extracted from TMPC films photooxidised at $\lambda > 300$ nm. Evolution of the spectra as a function of the pH.

Table 2
Decrease of absorbance at 1713 cm^{-1} provoked by MeOH treatment

Pre-irradiation duration (h)	PC	TMPC
50	−0.01	−0.29
100	−0.07	−0.47
150	−0.14	−0.63

Table 2 shows the decrease in absorbance at 1713 cm^{-1} generated by methanolic treatment as a function of the duration of pre-irradiation of PC and TMPC films. The data indicate that the amount of low molecular species extracted from oxidised films is higher in TMPC than in PC.

The UV–visible spectra of the solution after extraction of the low molecular weight products of TMPC are shown on Fig. 10. The pH of the extraction solutions is 5.1 for TMPC, compared to 6.4 for PC, confirming that more acidic species have been extracted from TMPC films.

The UV spectrum of the extracted solution can be modified after addition of NaOH (pH = 11.3). The maxima observed at 285, 306 and 343 nm in TMPC suggest the presence of phenolic structures among the extracted photoproducts. A confirmation of these phenolic structures was obtained by the measurement of the fluorescence of the methanolic solution. It revealed the presence of a fluorescent species at 400 nm under excitation at 310 nm.

The chromatograms of the methanolic solutions used to extract the oxidised species revealed the presence of a large variety of UV absorbing and fluorescent low molecular weight photoproducts.

3.3. Chemical treatments of photooxidised samples

Peroxidic groups were titrated by chemical reactions and derivatisation reactions were used to selectively convert specific oxidation products in groups easier to identify by infrared spectrometry.

3.3.1. Titration of hydroperoxides

Fig. 11 shows the results of the chemical titration of peroxidic species for photooxidised TMPC and PC films (thickness 20 μm).

The peroxidic species concentration is higher for TMPC films than for PC films.

Hydroperoxides are known to be thermally unstable at high temperature whilst peroxides are known to exhibit higher thermal stability. This property has been used to evaluate the respective concentration of hydroperoxides and peroxides formed in TMPC. Photooxidised samples were submitted to thermolysis at 100 °C for 24 h before titration in a second experiment. The participation of peroxides to the whole peroxidic groups concentration is observed to be close to 10%. This result is in good accordance with a previous paper in which peroxidic species have been titrated in thermooxidised films [5].

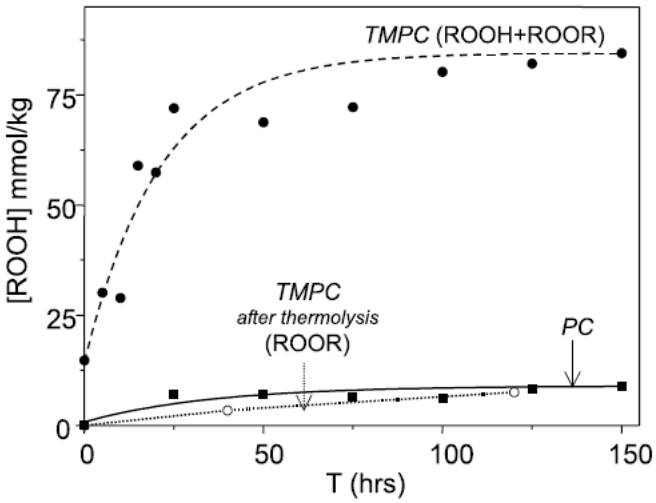


Fig. 11. Hydroperoxidic groups concentration as a function of irradiation time in PC and TMPC films (20 μm) photooxidised at $\lambda > 300$ nm.

Table 3
Changes of absorbance of the acyl fluoride bands after SF_4 treatment

Pre-irradiation duration (h)	PC 1810 cm^{-1}	TMPC 1815 cm^{-1}	PC 1840 cm^{-1}	TMPC 1840 cm^{-1}	PC 1810/1840 cm^{-1}	TMPC 1815/1840 cm^{-1}
50	0.06	0.35	0.04	0.17	1.35	2.07
100	0.16	0.49	0.11	0.26	1.45	1.90
150	0.26	0.61	0.18	0.32	1.43	1.90

3.3.2. SF_4 treatment

These reactions were carried out by submitting oxidised samples to SF_4 gas. The reaction is not quantitative as the hydroxyl absorption is not completely lost even after long duration treatments (300 h). Derivatives formed by reaction of SF_4 with aliphatic and aromatic carboxylic acids are characterised by a distinct C=O absorption [7,8]: aliphatic derivatives are observed at 1840–1845 cm^{-1} and aromatic or unsaturated derivatives are observed at 1810–1815 cm^{-1}.

SF_4 treatments of polycarbonate films irradiated 50, 100 and 150 h were carried out. On the IR spectra of all the so-treated films, the development of two absorption bands at 1810 and 1840 cm^{-1}, coming with a decrease of the carbonyl absorption and the elimination of the carbonyl absorption band at 1713 cm^{-1} was observed.

These experiments show that both aromatic and aliphatic carboxylic acids are formed in photooxidised polycarbonate films. Aromatic carboxylic acid structures with IR absorption in the range 1690–1700 cm^{-1} (1696 cm^{-1} for benzoic acid) account for part of the carbonyl absorption that gives the derivative band at 1810 cm^{-1}. Aliphatic acids with IR absorption at 1713 cm^{-1} give the derivative band at 1840 cm^{-1}.

Results of SF_4 treatments of TMPC and PC films throughout irradiation are reported in Table 3.

These results show that the whole concentration of acidic species increases with irradiation time and is always more important in TMPC than in PC. The ratio of the intensities of the band at 1815 cm^{-1} and at 1840 cm^{-1} is observed to be higher in TMPC films. These results mean that the accumulation of aromatic carboxylic acids is favoured in TMPC compared to PC.

Thermooxidised PC and TMPC films were submitted to gaseous SF_4. No derivative band of carboxylic acids was observed in PC treated films. SF_4 treatments of TMPC films involved the decrease of the band at 1696 cm^{-1} accompanied by the formation of a derivative band at 1815 cm^{-1}. The absorbance at 1704 cm^{-1} remained unchanged after SF_4 treatment.

It may be unambiguously concluded that no aliphatic carboxylic acids accumulate in thermooxidised films. In TMPC thermooxidised films, only aromatic acids are detected and the IR band at 1696 cm^{-1} may be attributed to the absorption of a benzoic acid type-compound.

3.3.3. NH_3 treatment

NH_3 treatments were carried out on photooxidised TMPC and PC films. NH_3 reaction led to a decrease in the carbonyl absorption region between 1800 and 1700 cm^{-1} with, among others, the disappearance of the band at 1713 cm^{-1} and the formation of a maximum around 1570 cm^{-1}. This maximum corresponds to the carboxylate ions band ($RCOO^-NH_4^+$) obtained by neutralisation of carboxylic acids. A weaker band with a maximum around 1660 cm^{-1} fits with the absorption of amide groups resulting from the reaction of esters with NH_3. The concentration of ester groups in both PC and TMPC was observed to remain fairly low.

NH_3 treatments were also carried out on thermooxidised TMPC films. Reaction of TMPC films with NH_3 led to a rapid decrease of the band at 1696 cm^{-1} ("benzoic acid") giving carboxylate ions ($RCOO^-NH_4^+$) bands, observed at 1587 and 1546 cm^{-1}. The product absorbing at 1704 cm^{-1} reacted more slowly with NH_3 leading to the formation of imines (–C=NH) detected at 1684 cm^{-1}. As previously suggested in the case of the photooxidation of polyparaxylylene [12], the band at 1704 cm^{-1} may be attributed to a benzaldehyde type-structure (1702 cm^{-1} for benzaldehyde). The reaction with NH_3 led also to the development of a broad absorption between 3300 and 2500 cm^{-1} with a maximum at 3200 cm^{-1} attributed to N–H vibrations.

3.4. Comparison of the rate of photoproducts formation in TMPC and PC

Fig. 12 shows the variation of absorbance in the carbonyl region as a function of irradiation time (a) and as a function of thermooxidation duration (b). It appears clearly that the rate of degradation is much higher for TMPC than PC. The variations of absorbance at 450 nm were also plotted as a function of irradiation time. The rate of yellowing was found to follow the same trend as the one observed for the changes measured in the IR domain.

These results suggest that *ortho*-methyl substitution on the phenyl rings is the source of much more oxidation than the methyl groups of the isopropylidene moieties.

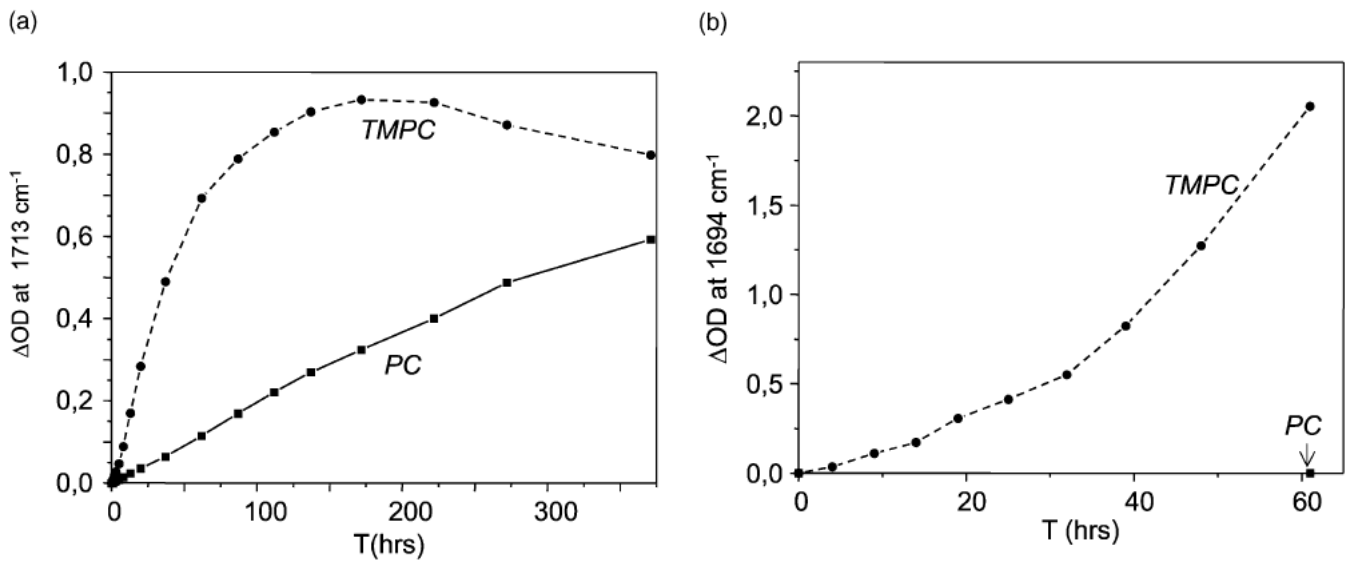


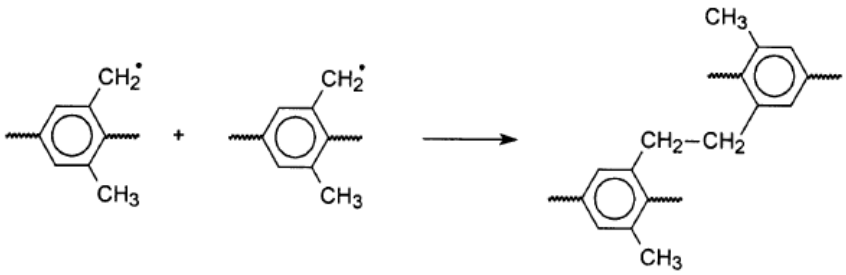
Fig. 12. Increase of the absorbance at 1713 cm^{-1} for PC and TMPC films as a function of photooxidation time at $\lambda > 300$ nm (a) and increase of the absorbance at 1696 cm^{-1} for PC and TMPC films (b) as a function of thermooxidation duration at 170 °C.

4. Discussion

Direct excitation of the chromophores of polycarbonate requires wavelengths shorter than 330 nm. TMPC is consequently directly accessible to UV light present in terrestrial solar radiation. As a result of the excitation by the shortest wavelengths of the sunlight, the scission of the CO–O bonds occurs.

Since the four *ortho*-methyl substituants of the phenyl rings of TMPC prevent from photo-Fries rearrangements, the macroradicals formed by CO–O bonds scission may recombine together before or after decomposition through decarbonylation or decarboxylation. The various resulting products identified as L_3 in PC [4] are formed in fairly low concentration in TMPC and are observed by IR spectrometry in the hydroxyl region at 3530 cm^{-1} (hydroxylated biphenyl structures). These species or the products resulting from their photolysis are largely responsible for the yellow discolouration of TMPC films under non-oxidative conditions.

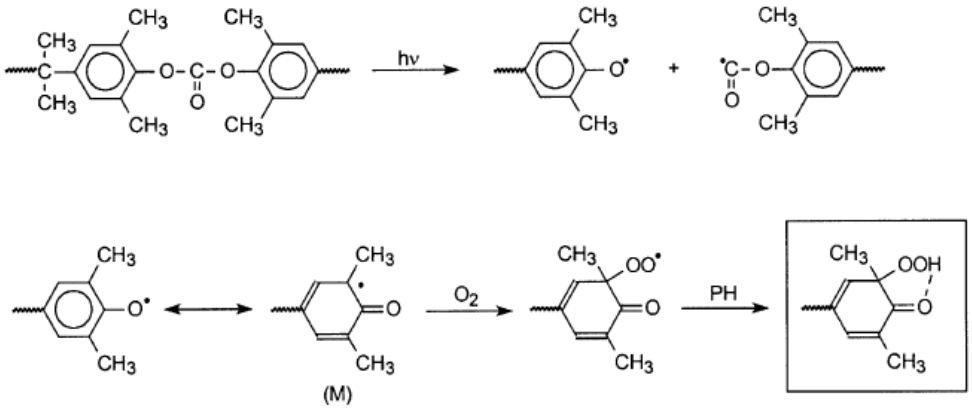
Macroradicals may also react separately by hydrogen abstraction on the methyl groups of the polymer leading to the formation of phenols as end-groups. The abstraction of a hydrogen atom on the *o*-CH_3 substituants leads to the formation of primary benzyl radicals (as previously shown in Scheme 2. In the absence of oxygen, the primary radicals may recombine together:



Scheme 6

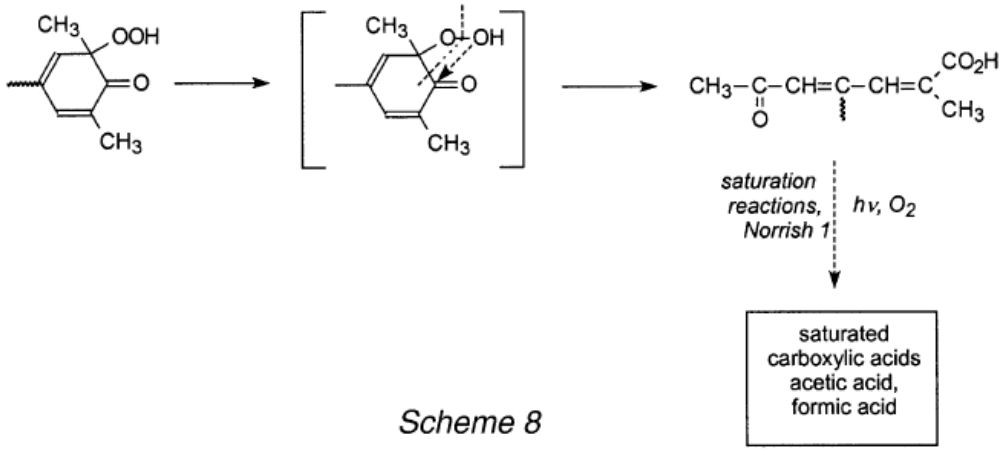
Such recombination leads to the crosslinking of the material evidenced by the measurement of an insoluble fraction and the increase in M_w of the TMPC films irradiated in vacuum.

When irradiation is carried out in the presence of oxygen, the oxidation of macroradicals formed in direct photoscission may also occur in parallel to recombination or hydrogen abstraction. The oxidation in a mesomeric form (M in Scheme 7) of phenoxy radicals has been shown in the case of poly(phenylene oxide) [13] to lead after hydrogen abstraction to the formation of hydroperoxides stabilised by an intramolecular H bond:



Scheme 7

The decomposition of these hydroperoxides involves the cleavage of the aromatic rings. Further saturation and Norrish type 1 reactions conduct finally to saturated aliphatic carboxylic acids observed at 1713 cm^{-1}. Part of this absorption may be attributed to formic and acetic acids trapped in the matrix, but which can diffuse in the gas phase under heating:



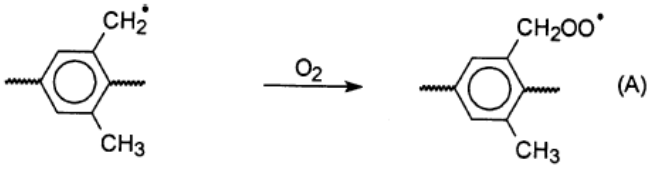
Scheme 8

Under irradiation in the presence of oxygen, primary macroradicals formed upon direct homolysis of the carbonate bond or their oxidative form are able to abstract the labile hydrogen atoms of the methyl groups, acting as initiators of the photooxidation of the methyl groups: the decrease in methyl groups content was measured to be important in photooxidation and insignificant in photolysis. As the rate of degradation of TMPC is observed to be much higher than that of PC, the hydrogen atoms in the *o*-CH_3 substituants have to be considered as the source of much more oxidation than the one on the methyl groups of the isopropylidene moieties.

As proposed in the previous paper [5] (Schemes 3–5), a possible route of photooxidation involves the isomerisation of the primary benzyl radicals to form more stable secondary radicals. The radicals obtained in this reaction may decompose by an oxidation leading to aromatic hydroperoxides that have been titrated. The hydroperoxides are photochemically unstable and can be decomposed to give quinone-methide (1655 cm^{-1}, 340 nm) and phenolic groups. In a detailed approach of the photodegradation of poly(phenylene oxide) recently published (the polymer also has *ortho*-methyl substituants on the aromatic ring), a similar mechanism was also proposed [13].

From the results of the identification of benzaldehyde (1704 cm^{-1}) and benzoic acid (1696 cm^{-1}) formed in photo- and in thermo-oxidation and the higher rate of network formation in photooxidation compared to photolysis, additional routes of oxidation of TMPC may be proposed.

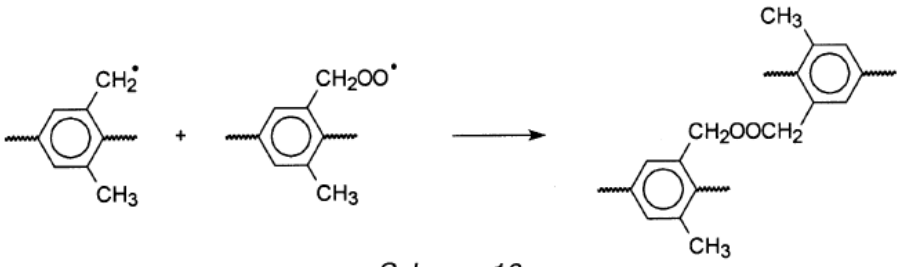
The oxidation of primary benzyl radicals may occur prior to isomerisation. A peroxy radical (A) is thus formed:



Scheme 9

The peroxy radical (A) obtained in this reaction may decompose in several ways:

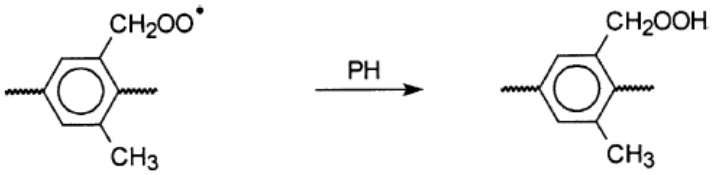
(1) A first route for the peroxy radical is a recombination with the primary benzyl radical. Such a process implies crosslinking which may account for the higher rate of the network formation in the presence of oxygen compared to vacuum exposure:



Scheme 10

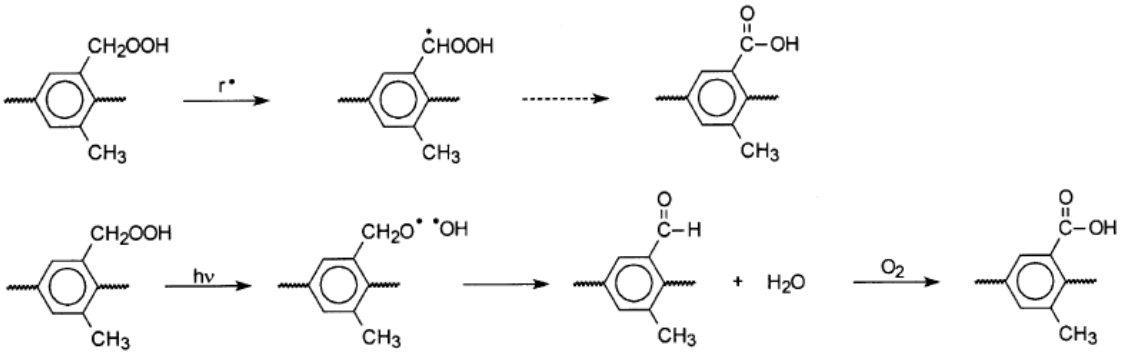
The peroxidic bridges thus formed account for the titration of peroxidic species in thermooxidation and in photooxised films submitted to thermolysis. The thermal instability of peroxide bridges above 140 °C accounts for the lower content in crosslinks measured in films thermooxidised at 170 °C.

(2) A second possibility is an hydrogen abstraction leading to primary hydroperoxides:



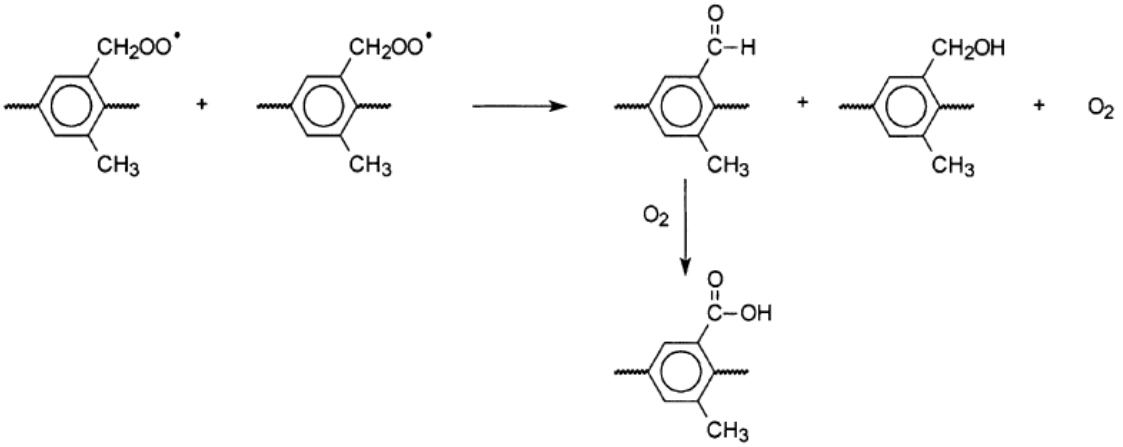
Scheme 11

The primary hydroperoxides are photochemically and thermally unstable, and may decompose to give a benzoic acid type product by a direct oxidation [14] or by an oxidation involving the formation of benzaldehyde further oxidised in benzoic acid:



Scheme 12

(3) The third route of decomposition is a disproportionation (Russell-type mechanism [15]) leading to the formation of alcohol and benzaldehyde also further oxidized in a benzoic acid type product:



Scheme 13

5. Conclusion

The analysis of the photoageing of polycarbonates points out the relationship between the chemical structure and the photochemical reactivity.

The objective of the ortho-substitution of the phenyl rings of PC was the inhibition of photo-Fries rearrangements. This benefit is counterbalanced by the fact that the methyl substituants of TMPC are the source of much more oxidation than the methyl groups of the isopropylidene moieties of PC. Methyl substituants are also involved in cross-linking reactions: the main feature occurring at low degree of conversion is the formation of a network after only a few hours of photooxidation.

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