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Comparison of the photochemical and thermal degradation of bisphenol-A polycarbonate and trimethylcyclohexane–polycarbonate

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Abstract

The photochemical and thermal behaviour of bisphenol-A polycarbonate (PC) and trimethylcyclohexane–polycarbonate (TMC–PC) have been compared. The ageing of films, irradiated at short ($\lambda = 254$ nm) and long ($\lambda > 300$ nm) wavelengths in the absence and in the presence of oxygen or thermo-oxidised at 170 °C, has been analysed by different spectroscopic and chromatographic methods. A dual photochemistry is shown to account for the photodegradation of TMC–PC, as previously reported for PC. Under excitation at the shortest wavelengths, the mechanism involves photo-Fries rearrangements of the aromatic carbonate units and a photo-induced oxidation of the aliphatic moieties. Under excitation at 254 nm, the second photo-Fries rearrangement is lowered in TMC–PC at the expense of the formation of yellowing structures. Moreover, under short and long wavelengths exposures, the rate of photo-oxidation of TMC–PC was observed to be higher than that of PC. Such effects have been attributed to a reduced mobility of the macromolecules and to a steric effect due to the trimethylcyclohexylidene structure that contains tertiary carbon atoms. Experimental results confirmed that, regarding oxidation which initially involves hydrogen abstraction, tertiary and secondary sites of TMC–PC are more oxidisable than the primary aliphatic ones contained in PC.

1. Introduction

One of the main features of trimethylcyclohexane–polycarbonate (TMC–PC) is the improvement of its heat resistance compared to that of bisphenol-A polycarbonate (PC). The substitution of the isopropylidene bridge of PC by a trimethylcyclohexylidene radical has been shown to increase the glass transition temperature of PC (150 °C) up to 239 °C [1].

The reactions that are produced by exposure of PC to solar light have been described by a dual photochemistry: direct phototransformation and photo-induced oxidation, with a ratio largely dependent upon the spectral distribution of the excitation light source [2–5]:

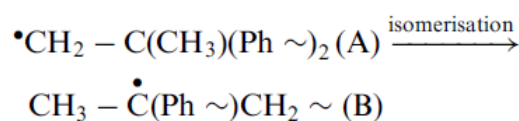
- Excitation of PC at short wavelength (e.g. 254 nm) involves mainly two consecutive photo-Fries rearrangements of the aromatic carbonate units leading successively to the formation of phenylsalicylate (L_1) and dihydroxybenzophenone (L_2) units as shown in Scheme 1. Photo-Fries products have been well defined by definite maxima in the UV and in the carbonyl range of the IR domain: L_1 at 320 nm and 1689 cm^{-1} and L_2 at 355 nm and 1629 cm^{-1} .

As a minor pathway, L_3 units are formed competitively to photo-Fries rearrangements: some radicals formed in CO–O bond scissions may decarbonylate or decarboxylate before further radical recombination or

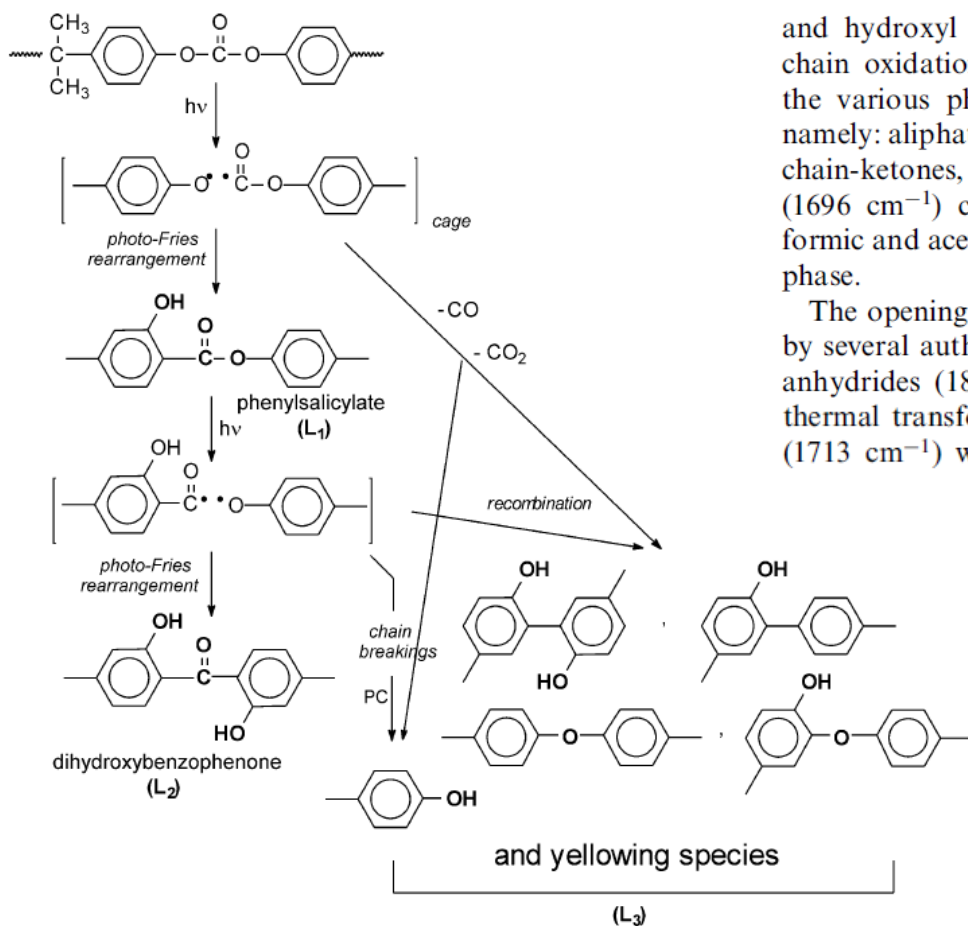
hydrogen abstraction. This leads to the formation of hydroxy- and dihydroxy-biphenyl units, aromatic ether structures and phenol as end-groups, further photolysed into a mixture of species (in a convoluted absorption) that produces the yellowing of the PC film without any defined structure.

- On irradiation at long wavelength (e.g. 365 nm) in the presence of oxygen, photoproducts have been shown to result mainly from the photo-induced oxidation on the gem dimethyl side-chain and from the phenyl rings oxidation. The various steps of the gem dimethyl side-chain photo-oxidation, initiated by photo-Fries process, are reported in Scheme 2.

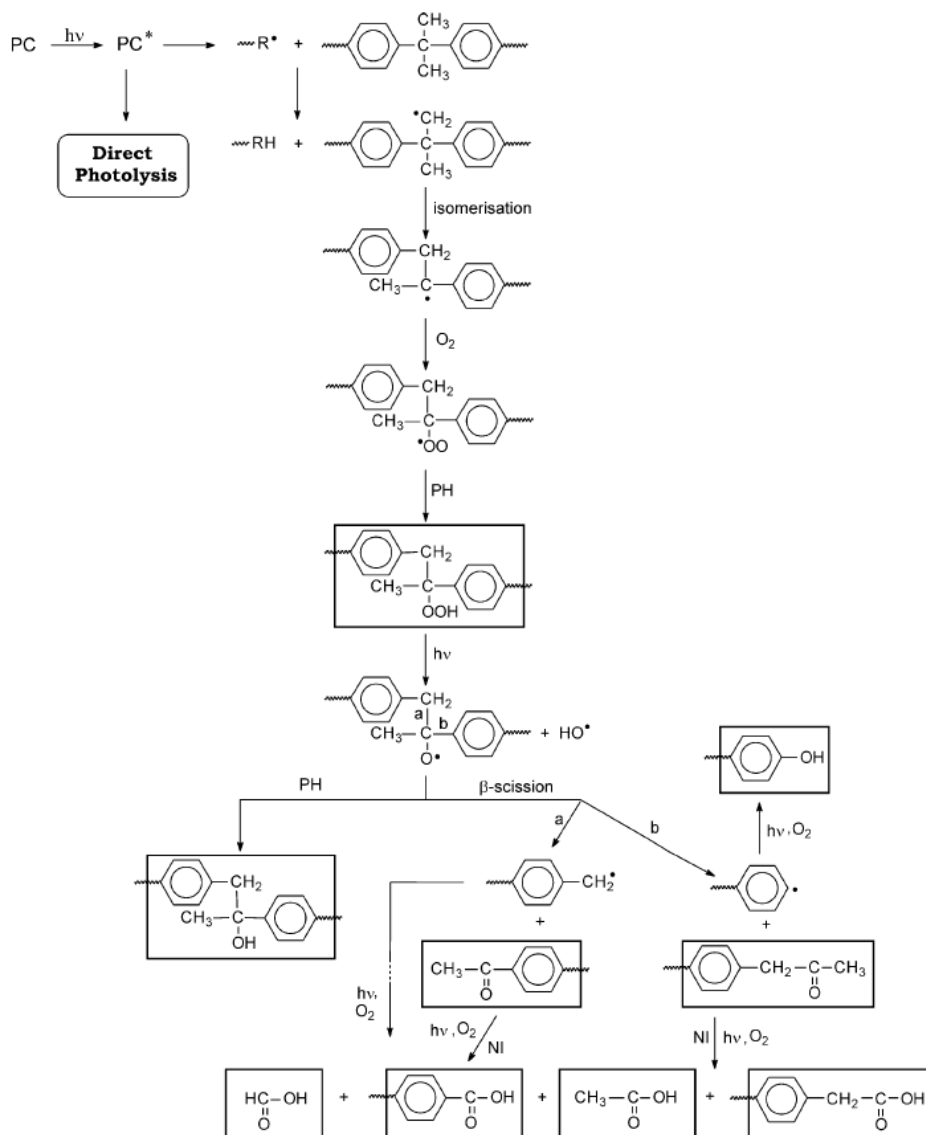
The first step of the oxidative reactions is an hydrogen abstraction on the polymeric backbone. Once formed, the primary methylene macroradicals (A) rearrange to yield the stable tertiary benzylic radicals (B):



The macroradical formed reacts with oxygen, leading to a peroxy radical that gives a hydroperoxide by abstraction of a labile hydrogen atom. Hydroperoxides decompose thermally or photochemically to give alkoxy



Scheme 1. Direct phototransformation of PC at short wavelength in the absence of oxygen.



Scheme 2. Gemdimethyl side-chain photo-oxidation of PC.

and hydroxyl radicals (which can mainly resume the chain oxidation reaction) leading to the formation of the various photoproducts that have been identified, namely: aliphatic (1724 cm⁻¹) and aromatic (1690 cm⁻¹) chain-ketones, aliphatic (1713 cm⁻¹) and aromatic (1696 cm⁻¹) chain-acids, chain-alcohols (3490 cm⁻¹), formic and acetic acid that are able to migrate in the gas phase.

The opening of phenyl rings of PC has been assessed by several authors [6]. It has been suggested that cyclic anhydrides (1860/1840 cm⁻¹) could be formed in the thermal transformation of dicarboxylic acid products (1713 cm⁻¹) which appear after phenyl ring scissions

under long-wavelength irradiation [2]. A probable mechanism of formation is reported in Scheme 3. The initiation steps by OH^\bullet and $^1\text{O}_2$ have been proposed by Clark and Munro [6].

- It has been shown that when PC is photo-oxidised under polychromatic light, provided by sources emitting short and long wavelengths radiations, the photochemical evolution of the polymer depends directly on the spectral distribution of the light [2]. This means that the ratio of short to long wavelengths determines the occurrence of direct phototransformation and side-chain photo-oxidation. Photo-Fries rearrangement is the main process occurring by absorption of radiations below 330 nm, whilst gemdimethyl side-chain and phenyl ring oxidation are provoked by radiations above 330 nm.

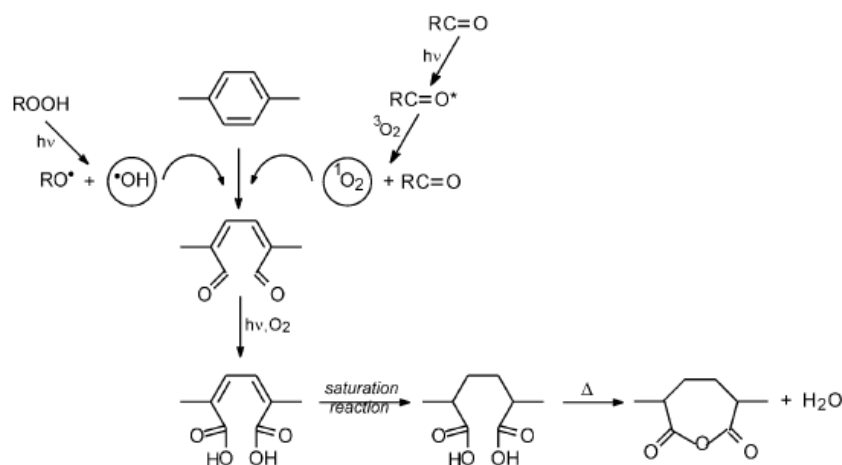
The first step of the oxidative reactions of polymers is an hydrogen abstraction on the polymeric backbone by a free radical formed by photonic excitation of chromophoric species. Two potential sites of abstraction exist on TMC-PC chain: the structure of TMC-PC has tertiary and secondary aliphatic carbons whilst that of PC contains only primary carbons. The rate of oxidation of TMC-PC, which contains more potentially reactive sites than PC, is therefore anticipated to be

higher than that of PC: such an hypothesis had to be checked.

The influence of the structure on the direct photochemistry at short wavelength also needs to be experimentally evidenced.

The two polymers were irradiated at short wavelength ($\lambda=254$ nm) and under polychromatic light ($\lambda>300$ nm) in the absence and in the presence of oxygen or thermo-oxidised at 170 °C. The photoproducts formed were characterised by UV-visible spectroscopy and fourier transform infra-red (FTIR) coupled with chemical derivatisation reactions, hydroperoxides titration, vacuum thermal treatments of oxidised films, size exclusion chromatography (SEC) and high performance liquid chromatography (HPLC) analysis after solvent extraction.

A detailed analysis of the products formed in each case of degradation is described in the present article. A comparison is made between the photochemical and thermal evolutions of PC and TMC-PC. The comparison of the behaviours in photo-oxidation and in thermo-oxidation is very helpful to elucidate the mechanisms of the thermodegradation. The main objective of this paper is to determine the validity of the mechanisms proposed for PC in the case of TMC-PC.



Scheme 3. Probable mechanism of ring oxidation.

2. Experimental

Non-stabilised PC and TMC-PC pellets were supplied by Aldrich and BASF (Germany) respectively. Thin films (20 μm) prepared for photodegradation experiments were obtained by evaporation of a polymer solution in CHCl_3 . Thick films (100–200 μm) prepared for thermo-oxidation experiments were obtained by compression moulding between PTFE-coated glass cloth at 200 bars for 90 s: at 280 °C for PC and at 300 °C for TMC-PC.

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 allowed irradiation at long wavelengths ($\lambda>300$ nm) [2]. Irradiations with monochromatic light at 254 nm were carried out in a SEPAP 254 unit [2]. Low temperature thermo-oxidation experiments were carried out in an aerated oven at 170 °C.

The macromolecular hydroperoxides formed in the photo-oxidised 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 allowed the in situ identification of carboxylic acids, esters, aldehydes and anhydrides [8,9].

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

IR spectra were recorded on a Nicolet 510 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 carried out by a technique described earlier [10]. Measurements were performed on a Nicolet 800 equipped with a NICPLAN microscope (liquid nitrogen-cooled MCT detector, 128 scan summations). The films were pressed between two polypropylene plates and were then sliced with a Reichert and Jung microtome. Slices with a thickness of ca. $50\text{ }\mu\text{m}$ were obtained and then examined through the FTIR microscope. The spectra were recorded every $10\text{ }\mu\text{m}$ from the irradiated surface towards the core of the sample.

HPLC analysis of the low molecular photoproducts, extracted by immersion of 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, $5\text{ }\mu\text{m}$ ($250 \times 4\text{ mm}$). The mobile phase was a gradient acetonitrile (Fisons HPLC solvent)–water (acidified with 2/1000 H_3PO_4). The outflow was 1 ml/min .

Average molecular weights (M_w) and molecular weight distribution (polydispersity index = M_w/M_n) of polymeric samples were obtained by SEC. SEC was carried out on a Waters 600 Controller using a 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 TMC–PC has been studied by measuring the density of solutions in CHCl_3 of the soluble part of irradiated samples according to a technique described earlier [11].

3. Photolysis at short wavelength ($\lambda = 254\text{ nm}$) in vacuum

On irradiation at short wavelength ($\lambda = 254\text{ nm}$) absorbed by the aromatic carbonate chromophoric groups, the photoreaction occurs only at the surface of PC and TMC–PC films. Absorption by polycarbonate at 254 nm has been computed as 90% of the incident light absorbed in the first $3\text{ }\mu\text{m}$. [2]

Photo-Fries rearrangements occurring in PC and TMC–PC films were monitored using UV and FTIR spectroscopies. In the first stages of photolysis of PC and TMC–PC, a main peak appears at 320 nm in the

UV range (Fig. 1) and at 1689 cm^{-1} in the carbonyl range of IR (Fig. 2), both attributed to the formation of the primary photo-Fries product L_1 .

L_1 is observed to reach a photostationary concentration and the photo-rearrangement of L_1 into L_2 accounts for the development of the bands at 355 nm and at 1629 cm^{-1} on the UV spectra (Fig. 1) and IR spectra (Fig. 2a) of PC, respectively.

If the IR band attributed to L_2 is observed to develop on the IR spectra of TMC–PC (Fig. 2b), however, surprisingly the maximum of the absorption band of L_2 at 355 nm is not observed on the UV spectra (Fig. 1) of TMC–PC.

At this stage of the analysis, the two following attempts, in order to explain this phenomenon, were not successful:

1. A matrix effect could have been an explanation since the mobility of macromolecular chain is reduced in TMC–PC compared to PC: the glass transition of TMC–PC ($239\text{ }^\circ\text{C}$) is quite higher than that of PC ($150\text{ }^\circ\text{C}$). To validate such an hypothesis, irradiation of PC and TMC–PC was carried out at 254 nm in degassed CHCl_3 solution. UV analysis of both irradiated solutions revealed the development of the absorption band of L_1 at 320 nm . As observed in rigid matrix, the maximum of the absorption band of L_2 at 355 nm is observed to develop on the UV spectra of PC solution and is not discerned on the UV spectra of TMC–PC solution. It is concluded that a matrix effect cannot account for the fact that the UV band of L_2 is not observed in TMC–PC photolysis.

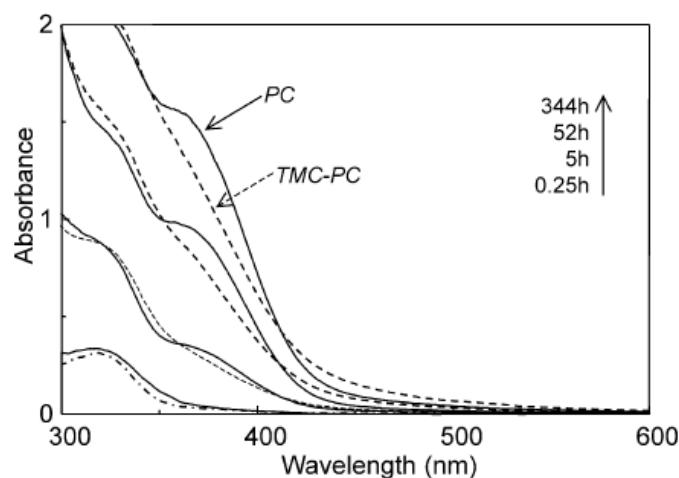


Fig. 1. Changes of the UV spectra (subtraction irradiated–non-irradiated sample) of PC film (—) and TMC–PC film (---) on photolysis at 254 nm .

2. A lower coplanarity of the dihydroxy-benzophenone system in TMC-PC compared to PC could have been another explanation. To determine the steric effect of the aliphatic moieties on the conjugated system, the benzophenone structure has been modelised for the two polycarbonates. The twisting angles between the two aromatic rings and the CO group have been determined by conformational searching using the Batchmin program within the MM2 force field of the Macromodel package [12]. The twisting angles were computed to be 28° in PC and 31.3° in TMC-PC. The consequence of this $3^\circ 3$ twist, when the isopropylidene moieties in PC are replaced by trimethylcyclohexylidene moieties in TMC-PC, can result only in a small shift of the maximum to shorter wavelength with a low decrease in the intensity [13]. It is not sufficient to engender the absence of the absorption band of L_2 .

The absorption band of L_1 observed in PC and in TMC-PC at 320 nm is progressively overlapped by an unstructured absorption. This absorption results from a mixture of species identified as L_3 on Scheme 1. L_3 units are formed competitively to the photo-Fries rearrangement and their formation accounts for the yellow color of the sample after irradiation.

In the hydroxyl region of the IR spectra of PC (Fig. 3a), the vibration bands observed to develop around 3547 cm^{-1} and at 3470 cm^{-1} are attributed respectively to the dimeric and polymeric OH stretching frequencies of the L_3 species. Most of the hydroxyl groups of photo-Fries products are intramolecularly bonded and observed at 3230 cm^{-1} .

In TMC-PC (Fig. 3b) an additional band is observed to develop with a low intensity at 3607 cm^{-1} that fits with the $\nu(\text{OH})$ band of non-hydrogen bonded phenol [14]. This result suggests that the presence of a labile hydrogen atom on the tertiary carbon atom of the trimethylcyclohexylidene structure of TMC-PC favors hydrogen abstraction by a phenoxy macroradical formed along with the O-CO bond scission. The macroradical yields phenol and no photo-Fries reaction occurs. In addition, the comparison of the shape of the hydroxyl absorption of the two polymers indicates that the contribution of dimer hydroxyl groups of L_3 at 3547 cm^{-1} to the whole absorption is slightly higher in TMC-PC than in PC.

The formation of L_1 , L_2 and L_3 involves ring substitution by hydroxyl groups that accounts for the development of the two bands at 1617 and 1585 cm^{-1} .

The concentration of photo-Fries products and yellowing L_3 species formed in TMC-PC and PC can be compared by measuring the variations of the absorbance at 1689 cm^{-1} (L_1), at 1629 cm^{-1} (L_2) and at 450 nm (L_3). The data obtained after 345 h exposure are reported in Table 1.

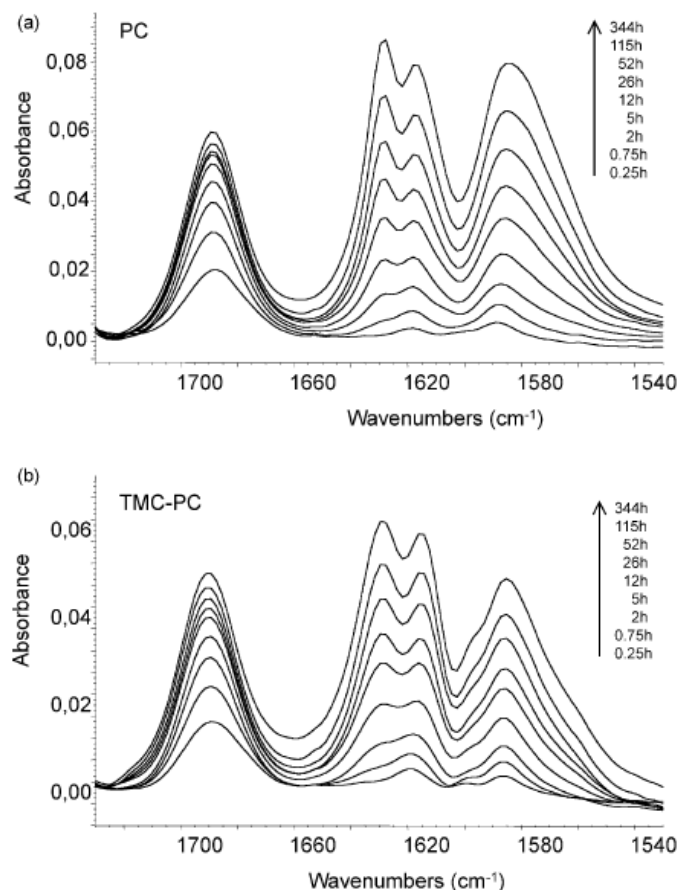


Fig. 2. FTIR spectra of (a) PC film and (b) TMC-PC film in the carbonyl region (irradiated—non-irradiated sample) for various photolysis times at 254 nm.

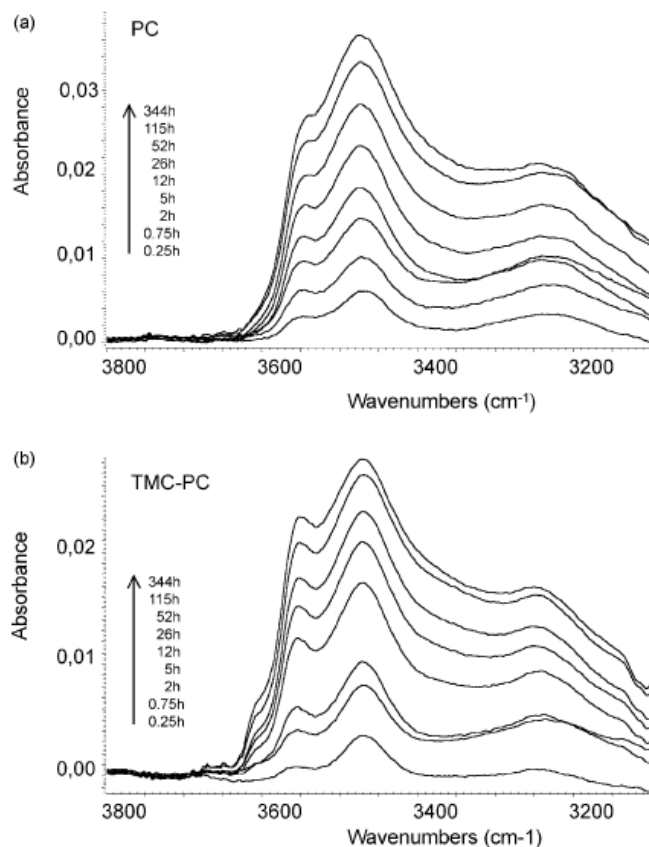


Fig. 3. FTIR spectra of (a) PC film and (b) TMC-PC film in the hydroxyl region (irradiated—non-irradiated sample) for various photolysis times at 254 nm.

As a complement, the absorption of L_2 (1629 cm^{-1}) is plotted on Fig. 4 as a function of the absorption of the yellowing L_3 species (450 nm) throughout exposure.

The analysis of Table 1 and Fig. 4 shows that the concentration of L_1 is roughly the same in the two polymers, the one of L_2 is slightly lower in TMC-PC compared to PC at the expense of yellowing L_3 species. This indicates that the photo-Fries rearrangement, and specially the conversion of L_1 to L_2 , is lowered at the expense of the formation of L_3 units in TMC-PC compared to PC.

Such differences between the two polymers imply that the second cage rearrangement in *ortho* position is more difficult in TMC-PC: it has been computed that the energy of the more stable L_2 conformation is 71 kJ/mol in PC and 148.7 kJ/mol in TMC-PC.

On the contrary the conversion of carbonate groups to L_3 photoproducts is favoured in TMC-PC, due to steric effects and to the presence of a labile hydrogen atom on the tertiary carbon atom. For comparison vacuum photolysis of PC and TMC-PC was carried out under irradiation at $\lambda > 300\text{ nm}$ in absence of oxygen. The yellowing of TMC-PC is also observed to be higher than that of PC.

The combination of these results may explain why the absorption band of L_2 at 355 nm is not observed in TMC-PC photolysis at 254 nm .

4. Photo-oxidation at short wavelength ($\lambda = 254\text{ nm}$)

Analysis by FTIR and UV spectroscopies indicates that the chemical changes in the presence or in the absence of oxygen during the first stages of exposure are the same. The IR spectra show that L_1 and L_2 are formed in both polycarbonates. L_2 is produced in lower proportion in TMC-PC than in PC. The corresponding maximum at 355 nm is observed only on the spectra of PC, as noticed previously for irradiation experiments in absence of oxygen. Although some differences can still be observed between oxygenated and vacuum exposures:

1. The absorption band of L_1 at 320 nm is more easily observed in photooxidative condition than in photolysis (Fig. 5). This is because during photolysis experiments the UV band of L_1 is overlapped by L_3 absorption whereas in photo-oxidation L_3 species are not observable. It has been shown that L_3 species are photo-oxidised under excitation in the presence of oxygen [2].

For the same reason no absorption maximum at 3607 cm^{-1} , corresponding to free hydroxyl groups of L_3 , is detected in the hydroxyl region of the IR spectra of TMC-PC.

2. As irradiation proceeds, the development of a sharp band at 1713 cm^{-1} (Fig. 6) and of a broad absorption around 3230 cm^{-1} are observed on the IR spectra of both polymers.

Table 1
Increase of absorbance measured after 345 h exposure at 254 nm

IR and UV-visible measurements	L_1 (1689 cm^{-1})	L_2 (1629 cm^{-1})	L_3 (450 nm)
PC	0.056	0.083	0.096
TMC-PC	0.053	0.065	0.154

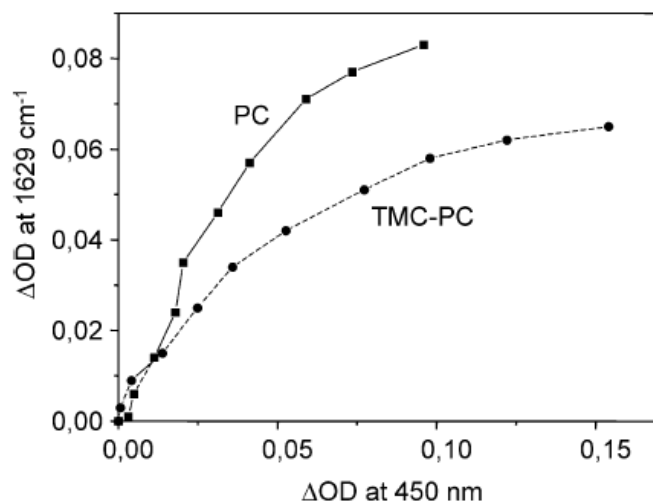


Fig. 4. Increase of the absorbance at 1629 cm^{-1} as a function of the increase of the absorbance at 450 nm for PC and TMC-PC films.

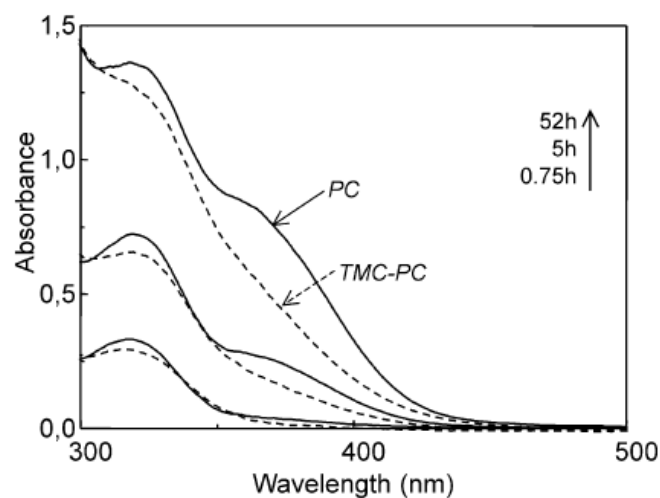


Fig. 5. Changes of the UV spectra (subtraction irradiated—non-irradiated sample) of PC film (—) and TMC-PC film (---) on photo-oxidation at 254 nm .

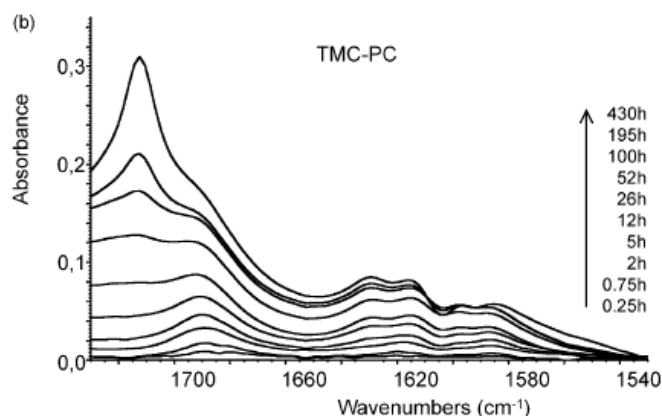


Fig. 6. FTIR spectra of (a) PC film and (b) TMC-PC film in the carbonyl region (irradiated—non-irradiated sample) for various photo-oxidation times at 254 nm .

By mean of SF₄ treatments, these two vibrations have been attributed in PC to the formation of molecular acetic and formic acids that are trapped in the PC matrix [2]. These acids have been shown to be final photoproducts formed in the photo-induced oxidation of the gemdimethyl side-chain.

The consequences of the treatments of photooxidized TMC-PC and PC films by SF₄ or by thermolysis under vacuum are observed to be analogous. The results allow the band at 1713 cm⁻¹ to be assigned to low molecular weight aliphatic carboxylic acid species in TMC-PC.

Fig. 7 shows the variations of absorbance at 1713 cm⁻¹ as a function of irradiation time. One can observe that the rate of formation of acid groups is two times higher for TMC-PC than PC.

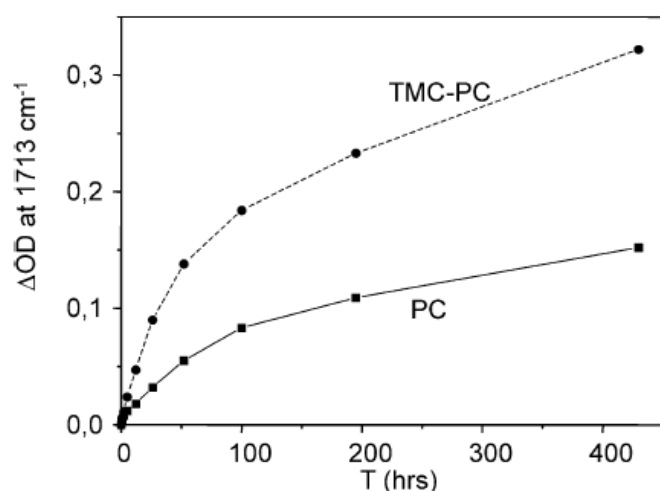


Fig. 7. Increase of the absorbance at 1713 cm⁻¹ for PC and TMC-PC films as a function of irradiation time at 254 nm.

It can be concluded from these experiments that the same photochemical mechanisms are involved under short wavelength exposure of PC and TMC-PC: direct phototransformation and photo-oxidation mechanisms.

However, the relative concentrations of the various photoproducts are found to be different in the two polymers. The second rearrangement in *ortho*-position is lowered in TMC-PC due to the reduced mobility and the steric effect of the trimethylcyclohexylidene structure. The presence in TMC-PC of tertiary carbons with more labile hydrogen atoms favors the formation of L₃ species in vacuum experiments and increases the rate of the photo-induced oxidation in aerated exposure.

5. Photo-oxidation at $\lambda > 300$ nm

5.1. Chemical changes in the solid polymers on exposure

5.1.1. FTIR and UV-visible analysis

The light absorption by the carbonate chromophoric units extends up to 330 nm. This makes PC, as well as TMC-PC, directly accessible to UV light present in terrestrial solar radiation.

The photo-oxidation of TMC-PC and PC at $\lambda > 300$ nm leads to noticeable modifications of the UV and IR spectra of irradiated films.

In the UV-visible (Fig. 8), the absorption of L₁ is observed to develop at 320 nm for short exposure time of both polycarbonates. The first photo-Fries rearrangement is the initial photochemical process involved in the long wavelengths photo-oxidation of both polymers.

As irradiation proceeds, the band of L₁ is rapidly overlapped by an unstructured absorption at wavelengths below 500 nm, which has been attributed to a mixture of colored species formed in ring oxidation [4,5].

In the carbonyl region (Fig. 9) the photo-oxidation leads, at low conversion, to the formation of absorption bands with the same maxima as reported above for the short wavelength irradiation and that account for photo-Fries rearrangement: L₁ at 1689 cm⁻¹, L₂ at 1629 cm⁻¹ and ring substitutions at 1617 and 1585 cm⁻¹.

As photo-oxidation proceeds, the hydroxyl and carbonyl absorption broaden and several bands with definite maxima are observed to develop on the IR spectra at 1690, 1713, 1724, 1840 and 1860 cm⁻¹.

In the hydroxyl region (Fig. 10), the appearance of broad absorption bands are observed with maxima around 3470 and 3330 cm⁻¹. These absorptions account

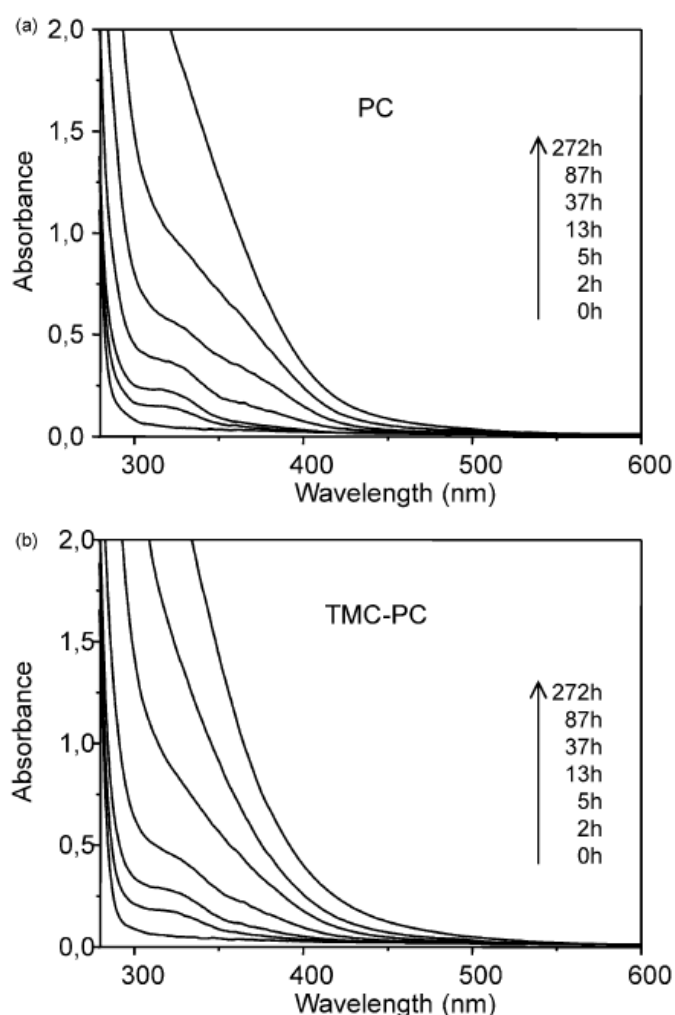


Fig. 8. Changes of the UV spectra of (a) PC film and (b) TMC-PC film on photo-oxidation at $\lambda > 300$ nm.

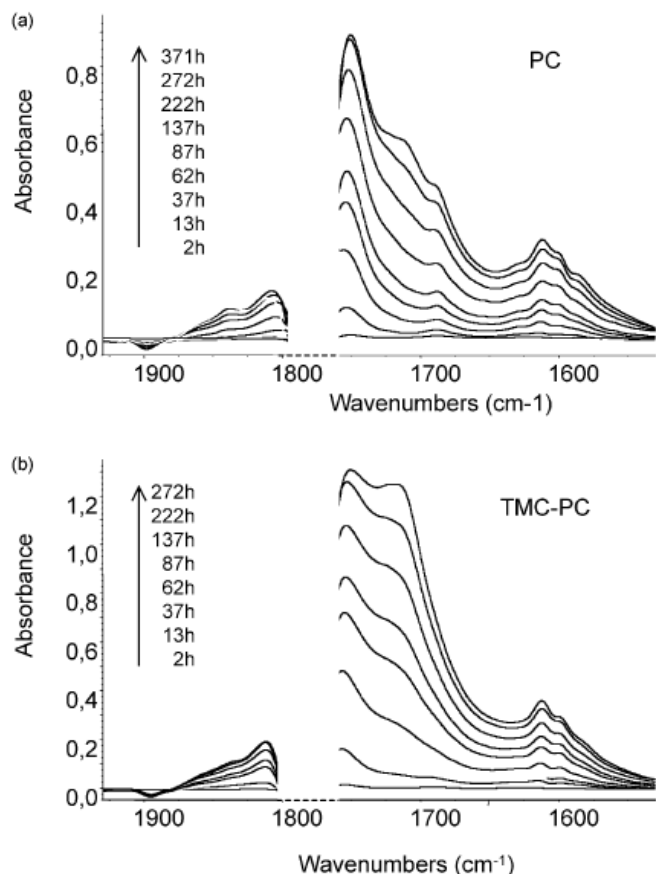


Fig. 9. FTIR spectra of (a) PC film and (b) TMC-PC film in the carbonyl region (irradiated—non-irradiated sample) for various photo-oxidation times at $\lambda > 300$ nm.

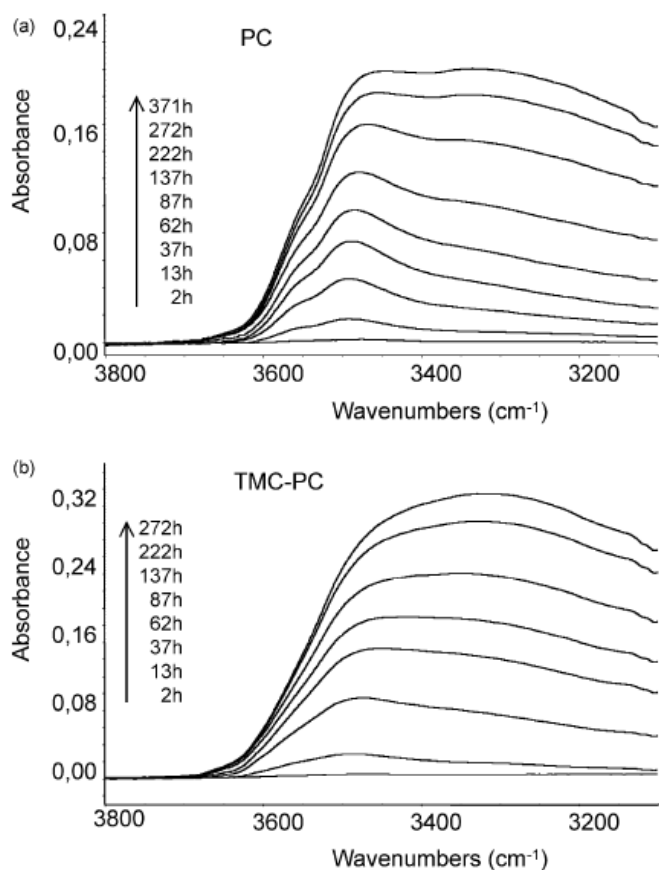


Fig. 10. FTIR spectra of (a) PC film and (b) TMC-PC film in the hydroxyl region (irradiated — non-irradiated sample) for various photo-oxidation times at $\lambda > 300$ nm.

respectively for the formation of bonded alcohols and carboxylic acids.

The assignment of all the maxima to precise chemical structures was performed by means of derivatisation reactions, methanolic and thermal treatments.

5.1.2. Spatial distribution

A thick film (100 μm) of TMC-PC was irradiated for 100 h. The oxidation profile is determined by recording the spectra every 11 μm . The increase of absorbance in the hydroxyl range is plotted on Fig. 11 as a function of the distance from the exposed face.

The oxidation photoproducts appear to be distributed heterogeneously in the TMC-PC sample as previously observed for PC [2]. Only the top 60 μm of films are affected by irradiation.

The degradation profile exhibits the same shape under vacuum and aerated exposures. The fact that oxidation is confined to the first 60 μm is then related to the strong light absorption by the irradiated films.

5.1.3. Molecular weight changes upon irradiation

The evolution of the molecular weight (M_w) as a function of irradiation time is shown in Fig. 12.

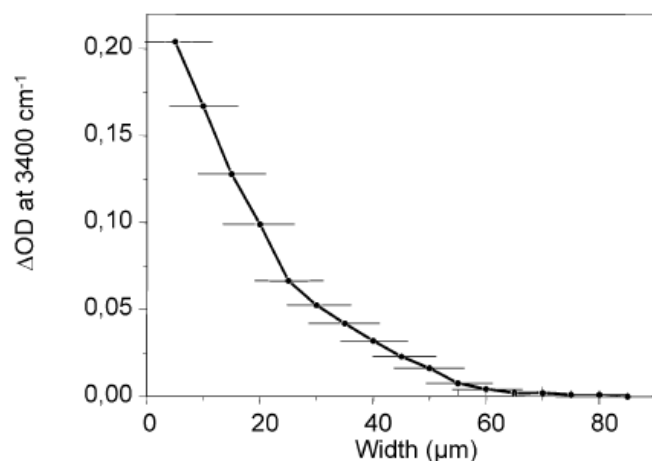


Fig. 11. Photo-oxidation profile measured by micro-FTIR spectroscopy of a TMC-PC film (100 μm) irradiated 100 h at $\lambda > 300$ nm.

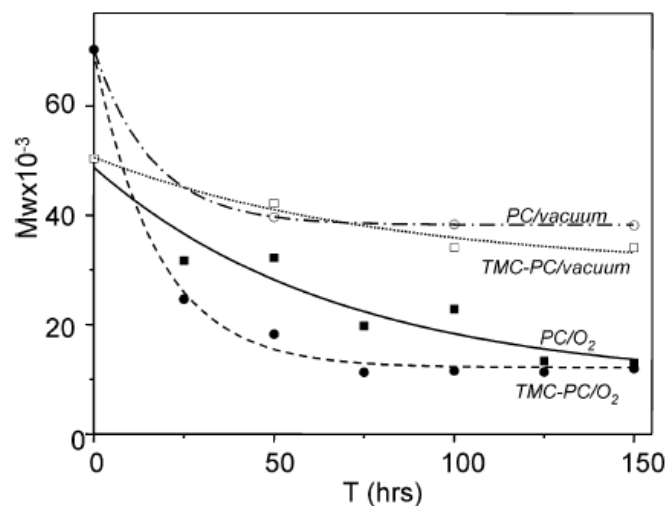


Fig. 12. Evolution of M_w of PC and TMC-PC films irradiated at $\lambda > 300$ nm as a function of irradiation time in the presence and in the absence of oxygen.

The M_w of films irradiated in presence and in absence of oxygen gradually decreases and reaches a limit with irradiation time. Chain scissions are observed to occur at larger extent in the presence than in the absence of oxygen.

The value of polydispersity index (M_w/M_n) determined throughout photo-oxidation, is reported in Table 2.

Non-irradiated polycarbonate films are soluble in CHCl_3 at room temperature. Irradiation of the polycarbonate films is observed to produce a portion of each sample that is insoluble in CHCl_3 . The amount of this insoluble material, measured by densimetry is reported in Table 3.

These data indicate that the decrease in M_w measured by SEC is the major phenomenon. In parallel, micro-gel formation by partial crosslinking of irradiated films also occurs at much lower extent. Main-chain scissions are prevalent on crosslinking during the course of the photo-oxidation of both polycarbonates.

5.1.4. Kinetic study of the photo-oxidation

Fig. 13 shows the variations of absorbance at 1713 cm^{-1} as a function of irradiation time. As observed previously under irradiation at 254 nm , the rate of photo-oxidation is much higher for TMC-PC than PC.

The variation of absorbance at 450 nm has also been plotted as a function of irradiation time. The rate of yellowing is found to follow the same trend (rate of yellowing higher in the case of TMC-PC).

5.2. Chemical treatments of photo-oxidised samples

Peroxidic groups were chemically titrated and derivatisation reactions were used to selectively convert oxidation products into groups which are more easily identified by FTIR.

5.2.1. Titration and identification of hydroperoxides

Fig. 14 shows the variations of concentration of hydroperoxides for irradiated TMC-PC and PC films (thickness $20\text{ }\mu\text{m}$).

The results show that the hydroperoxides concentration is much higher for TMC-PC films than for PC films. The same trend has been reported above for carbonyl photoproducts (see Fig. 13).

Alcohols and hydroperoxydes can be converted into nitrites and nitrates respectively by reaction with gaseous NO in the absence of oxygen. Completeness of reaction was not possible because NO has the undesirable effect to react with carbonate units. Therefore only qualitative data have been obtained. NO treatments of irradiated TMC-PC and PC films revealed the formation of nitrate absorption bands at 1300 and 1630 cm^{-1} attributed to derivatives of tertiary hydroperoxydes [15] associated with a partial loss in hydroxyl absorption around 3470 cm^{-1} . The two derivatives bands are not observed in NO treatments of non-irradiated films. No secondary or primary nitrate were detected. It may be therefore concluded that the main site of hydroperoxidation in both polycarbonates is a tertiary carbon atom.

Table 2
Changes in (M_w/M_n) determined by SEC

Irradiation time(h)	PC	TMC-PC
0	2.7	7.7
25	9.4	11.5
50	7.3	12.7
75	10.3	11.0
100	10.5	19.0
125	11.0	18.0
150	10.8	19.5

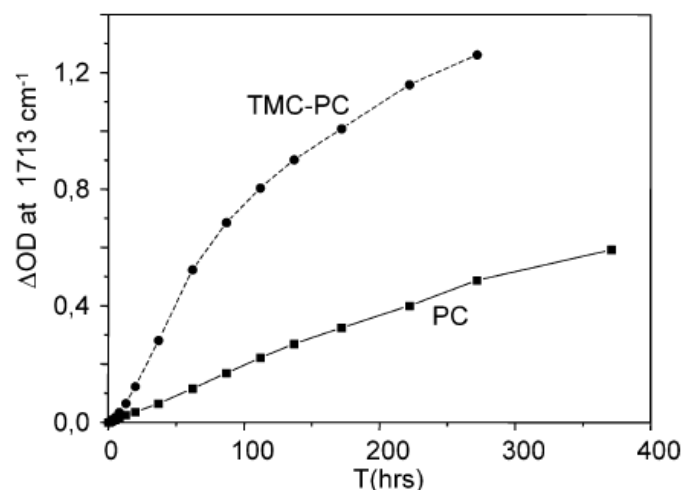


Fig. 13. Increase of the absorbance at 1713 cm^{-1} for PC and TMC-PC films as a function of irradiation time at $\lambda > 300\text{ nm}$.

Table 3
Changes in solubility determined by densimetry

Irradiation time(h)	PC (%)	TMC-PC (%)
0	100	100
15	93	96
50	90	94
100	90	94
150	89	93

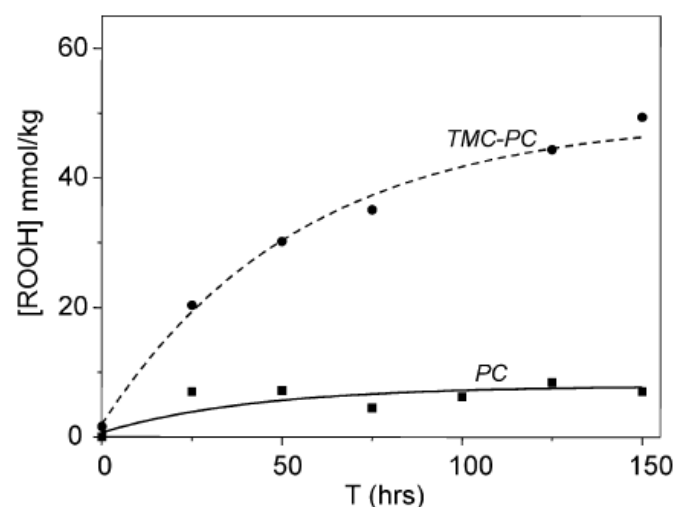


Fig. 14. Hydroperoxy groups concentration as a function of irradiation time in PC and TMC-PC films photo-oxidised at $\lambda > 300\text{ nm}$.

Table 4
Absorbance of the acyl fluoride bands after SF₄ treatment

Irradiation duration (h)	PC (1810 cm ⁻¹)	TMC-PC (1810 cm ⁻¹)	PC (1840 cm ⁻¹)	TMC-PC (1840 cm ⁻¹)	PC (1840/1810 cm ⁻¹)	TMC-PC (1840/1810 cm ⁻¹)
50	0.06	0.19	0.04	0.18	0.66	0.95
100	0.16	0.40	0.11	0.33	0.69	0.82
150	0.26	0.48	0.19	0.43	0.73	0.90

5.2.2. SF₄ treatment

The reactions were carried out by submitting the photo-oxidised samples to SF₄ gas. Derivatives formed by reaction of SF₄ with aliphatic and aromatic carboxylic acids are characterised by a distinct C=O absorption [8,9]: aliphatic derivatives at 1840–1845 cm⁻¹ and aromatic and unsaturated derivatives at 1810–1815 cm⁻¹.

SF₄ treatments of polycarbonate films irradiated for 50, 100 and 150 h lead to 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.

These results indicate that both aromatic and aliphatic carboxylic acids are formed in photo-oxidised 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 carboxylic acids with IR absorption at 1713 cm⁻¹ generate the derivative band at 1840 cm⁻¹.

The elimination of the acidic absorption allows the observation, on the IR spectra of both treated polymers, of unreacting bands at 1724 and 1690 cm⁻¹ that have been attributed respectively to aliphatic and aromatic ketones groups in PC [2].

Results of SF₄ treatments of TMC-PC and PC films pre-irradiated 50, 100 and 150 h are reported in Table 4.

These results show that the whole concentration of acidic species increases with irradiation time and is always superior in TMC-PC than in PC films. The ratio of the intensities of the band at 1840 and at 1810 cm⁻¹ is observed to be higher in the TMC-PC films. It can be deduced that the accumulation of aliphatic carboxylic acids is favoured in TMC-PC compared to PC.

5.2.3. NH₃ treatment

NH₃ treatments were carried out on photo-oxidised TMC-PC and PC films. NH₃ reaction leads to a decrease in the carbonyl absorption region between 1800 and 1700 cm⁻¹ with, among others, the disappearance of a band at 1713 cm⁻¹ and the formation of a maximum around 1570 cm⁻¹. This maximum corresponds to the carboxylate ions band (RCOO⁻ NH₄⁺) obtained by neutralisation of carboxylic acids. A

weaker band with a maximum around 1660 cm⁻¹ corresponds to the absorption of amide groups resulting from the reaction of esters. The concentration of ester species in both polycarbonates is observed to remain fairly low.

5.2.4. Analysis of the volatile products

TMC-PC and PC films photo-oxidised for 50, 100 and 150 h were thermolysed at 100 °C in the absence of oxygen.

Vacuum heating leads to the decrease of the carbonyl absorption between 1800 and 1700 cm⁻¹ and to the disappearance of the band at 1713 cm⁻¹ (acids); a broad decrease of the hydroxyl absorption is noticed throughout the thermolysis. In parallel, thermal treatments induce the development of a vibration band at 1840 cm⁻¹ with a shoulder at 1860 cm⁻¹ (anhydrides [2]).

In the domain of hydroxyl vibration, the broad decrease centred at 3230 cm⁻¹ (range of associated OH groups of acids) contributes for about 25% to the hydroxyl absorption.

Results of vacuum thermal treatments at 100 °C for 24 h of TMC-PC and PC films pre-irradiated 50 and 100 h are reported on Table 5.

The data of Table 5 indicate that carboxylic acids formed in PC and TMC-PC can be extracted at 100 °C and that the concentration of extractable acidic species is higher in TMC-PC than in PC. In both photo-oxidised polymers, a fraction of these acids are dicarboxylic species formed in ring opening which thermally cyclise to give anhydrides observed at 1840/1860 cm⁻¹. The other fraction of acidic species is composed of low molecular weight photoproducts, formed in aliphatic moieties oxidation, that can be lost by evaporation from the irradiated films. Table 5 shows that the concentration of these latter species is higher in TMC-PC.

Infra-red analysis of the composition of the gas phase was also 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 λ > 300 nm and the gas was periodically analysed by IR spectroscopy throughout exposure.

Table 5
Variation of absorbance upon thermal treatment

Pre-irradiation duration (h)	PC (1713 cm ⁻¹)	TMC-PC (1713 cm ⁻¹)	PC (1840 cm ⁻¹)	TMC-PC (1840 cm ⁻¹)	PC (1713/1840 cm ⁻¹)	TMC-PC (1713/1840 cm ⁻¹)
100	-0.02	-0.12	0.03	0.03	0.7	4.0
150	-0.06	-0.22	0.05	0.05	1.2	4.4

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

In the other regions of the IR spectra, the formation of small amounts of water and traces of carbonyl groups at 1794 and 1772 cm^{-1} are observed, which suggests the presence of gaseous formic and acetic acid in their dimer form, respectively.

This experimental result confirms that some of the aliphatic acid groups are low molecular weight compounds that can be lost by evaporation at 100 °C from both polycarbonate films.

From the remaining carbonyl absorption of photo-oxidised films, as previously observed after SF_4 treatment, bands at 1724 and 1690 cm^{-1} are observed on the IR spectra of both polymers. These bands can be respectively attributed to aliphatic and aromatic ketones.

5.2.5. Analysis of the extractable photoproducts

Immersion in methanol for 24 h of photo-oxidised films produces changes in the IR spectra that are analogous to those observed in thermal treatment at 100 °C. After methanolic treatments, a decrease of the carbonyl absorption between 1800 and 1700 cm^{-1} and the disappearance of the maximum at 1713 cm^{-1} are observed (Fig. 15).

Table 6 shows the decrease in absorbance at 1713 cm^{-1} generated by immersion of PC and TMC-PC films pre-irradiated 50 and 100 h. The concentration of low molecular weight species extracted from oxidised films is higher in TMC-PC than in PC.

Table 6
Decrease of absorbance at 1713 cm^{-1} provoked by MeOH treatment

Pre-irradiation duration (h)	TMC-PC	PC
50	-0.19	-0.01
100	-0.48	-0.07

The UV-visible spectra of the methanolic solution after extraction of the low molecular weight products are reported on Fig. 16. The pH of the extraction solutions is 6.4 for PC and 5.1 for TMC-PC confirming that more acidic species have been extracted from TMC-PC films.

The UV spectrum of the extracted solutions can be modified by addition of NaOH (pH = 11.3). Maxima are observed at 245, 284 and 330 nm in TMC-PC and at 243, 289 and 323 nm in PC suggesting the presence of phenolic structures among the extracted photoproducts. A confirmation of these phenolic structures has been obtained by measuring the fluorescence of the methanolic solution. It reveals 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 reveal the presence of a large variety of UV absorbing and fluorescent photoproducts. Polar and non-polar species have been extracted by methanol from oxidised films. A gradient

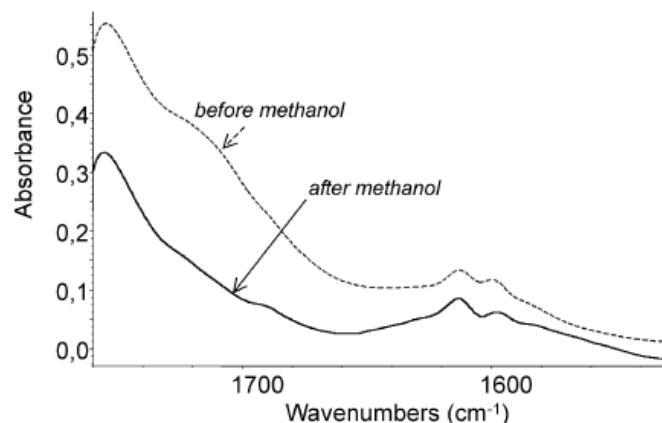


Fig. 15. Evolution of the IR spectra of a photo-oxidised TMC-PC film throughout post-immersion in methanol.

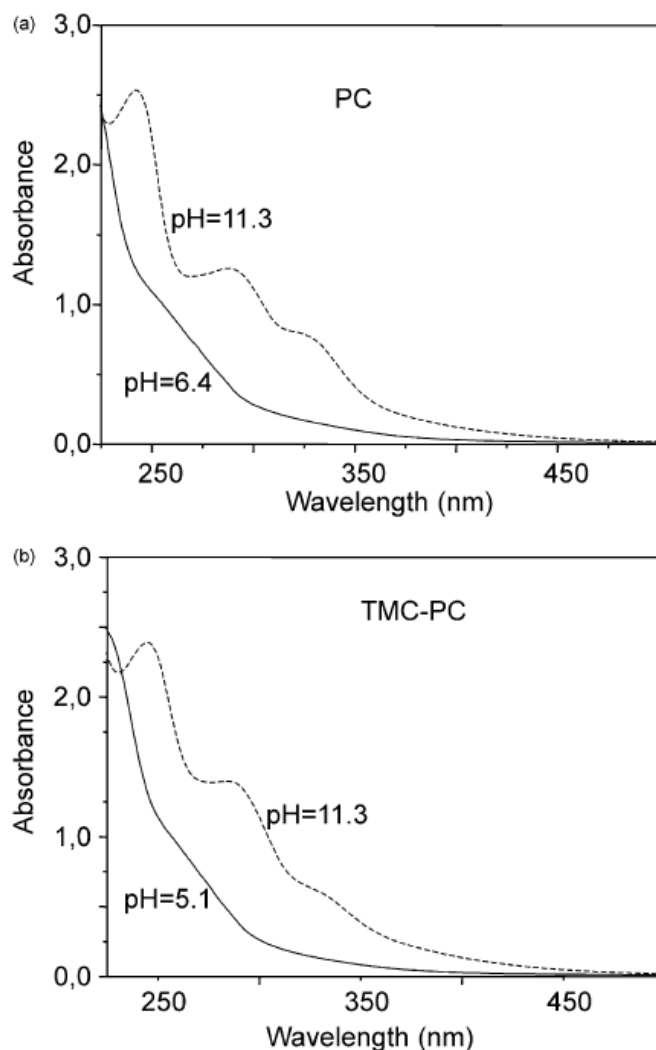


Fig. 16. UV-visible absorption spectra of the methanolic solution of the low molecular weight photoproducts extracted from (a) PC film and (b) TMC-PC film photo-oxidised at $\lambda > 300$ nm. Evolution of the spectra as a function of the pH.

of a mixture of $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ varying from (90/10)% to (10/90)% has been used to elute all the photoproducts.

The absorption and emission features of each fraction have been compared to those of model compounds analysed under the same conditions. The retention time, the absorption and the emission of some species are exactly fitting those of benzoic acid, 4-hydroxybenzoic acid, hydroquinone and phenol.

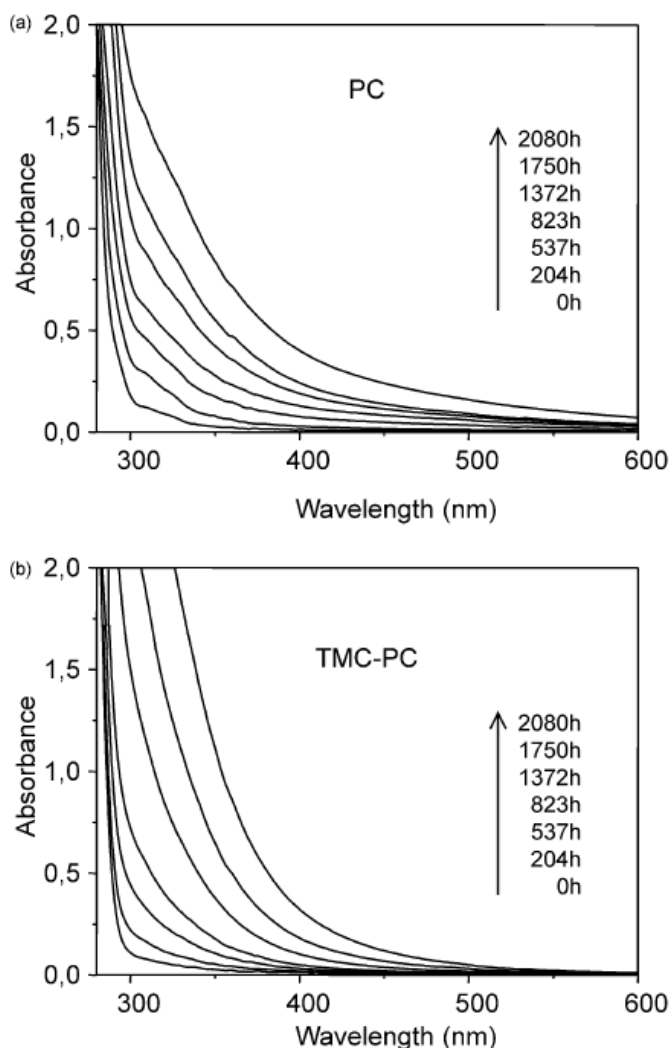


Fig. 17. Changes in UV spectra of (a) PC film and (b) TMC-PC film thermo-oxidised at 170 °C.

6. Thermo-oxidation at 170 °C

The thermo-oxidation of PC and TMC-PC films (130–150 μm) was carried out in an aerated oven at 170 °C.

The changes in UV-visible of PC and TMC-PC during the course of thermo-oxidation are shown in Fig. 17. An increase in UV-visible absorption of oxidised films without any defined maximum can be observed.

The changes that occur in the infrared carbonyl region of PC and TMC-PC are shown on Fig. 18.

Absorption bands with defined maxima are observed at 1690, 1724, 1840 and 1860 cm^{-1} . The maximum at 1724 cm^{-1} is not easily discerned in TMC-PC because it is overlapped by the formation of other carbonylated species. No band at 1713 cm^{-1} corresponding to acids is observable on the spectra. It is recalled that vacuum thermal treatment of photo-oxidised polycarbonate films leads to the elimination of the carboxylic acids.

The PC and TMC-PC thermo-oxidised films were submitted to gaseous SF_4 and NH_3 for better identification of the oxidation products. No absorption band resulting from the derivative of carboxylic acids was observed. It may be unambiguously concluded that, in conditions of thermo-oxidation at 170 °C, no carboxylic acids accumulate in the polymeric films.

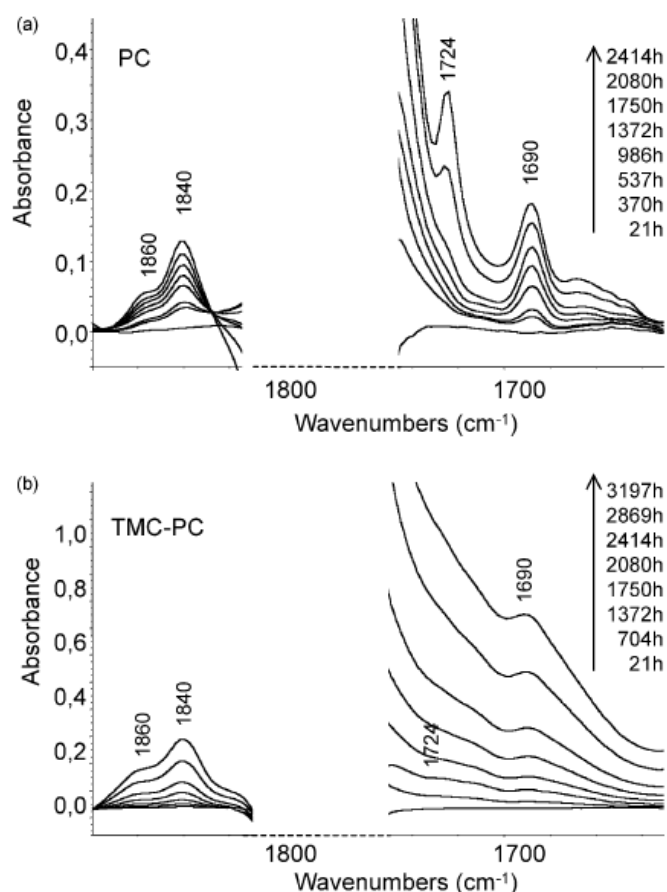


Fig. 18. Changes in the carbonyl region of IR spectra of (a) PC film and (b) TMC-PC film (thermo-oxidised at 170 °C).

No change is observed in the absorptions at 1724 and 1690 cm^{-1} after SF_4 and NH_3 treatment. This confirms the previous assignment of the maxima at 1724 cm^{-1} and 1690 cm^{-1} to aliphatic and aromatic ketones, respectively.

Moreover, no absorption band in the range 3300–3200 cm^{-1} (assigned to carboxylic acids) is observed in the spectra of thermo-oxidised PC and TMC-PC films (Fig. 19). Such an observation is in good accordance with the analysis of the carbonyl domain.

PC exhibits absorption bands at 3553 and 3514 cm^{-1} which are associated with the non-hydrogen bonded groups formed. In the OH region of TMC-PC there is an increase of a broader hydrogen-bonded absorption band centred at 3490 cm^{-1} . This observation confirms, in agreement with the complexity of the carbonyl IR envelope, the presence in TMC-PC of several oxidation products and that the reactions involved in TMC-PC are not simple.

The rate of formation of the products in the carbonyl region as a function of the duration of thermo-oxidation is given in Fig. 20. It is evident from the figure that the rate of thermo-oxidation of TMC-PC is much higher than that of PC. An analogous conclusion has been obtained by comparison of the rate of the yellowing of both polymers.

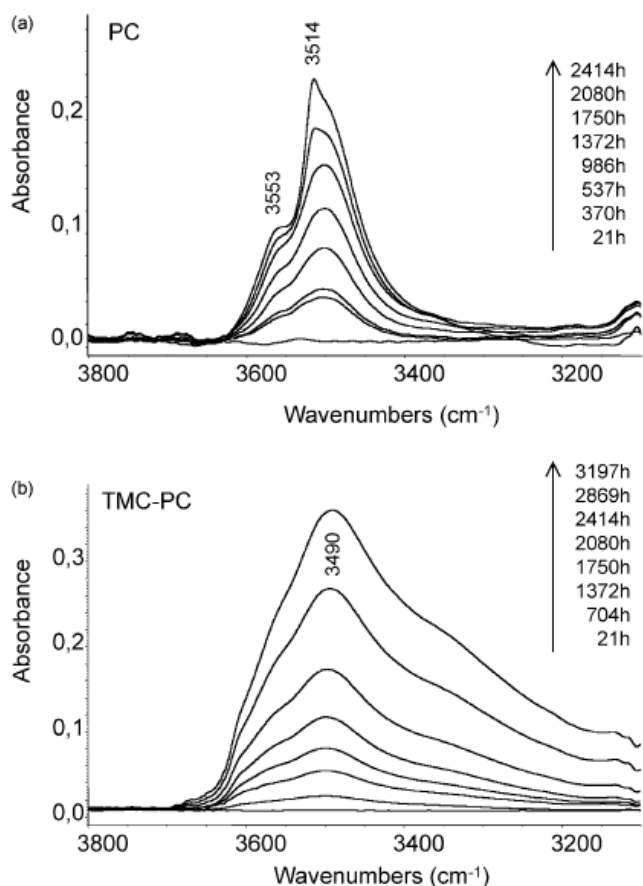


Fig. 19. Changes in the hydroxyl region of IR spectra of (a) PC film and (b) TMC-PC film thermo-oxidised at 170 °C.

The amounts of the insoluble material formed throughout thermo-oxidation of PC and TMC-PC films are reported in Table 7.

The evolution of the molecular weight (M_w) of PC and TMC-PC films as a function of thermo-oxidation duration is reported on Table 8.

These data indicate, as previously reported for the photo-oxidation (see Fig. 12 and Table 3), that the main-chain scission is the major phenomenon during the thermo-oxidation experiments of both polycarbonates.

7. Discussion

The results of the analysis of the photochemical and thermal degradation of TMC-PC can be interpreted as follows.

PC and TMC-PC are directly accessible to UV light present in terrestrial solar radiation. As a result of the excitation by the shortest wavelengths radiations of the sunlight, photo-Fries rearrangements may occur leading to the formation of L_1 (1689 cm^{-1} , 320 nm) as observed by FTIR and UV-visible spectroscopies (Scheme 1).

In the absence of oxygen a second photo-Fries rearrangement may occur leading to the formation of L_2 (1629 cm^{-1} , 355 nm).

The radicals resulting from the CO-O bond scissions may also recombine together before or after decomposition through decarbonylation or decarboxylation.

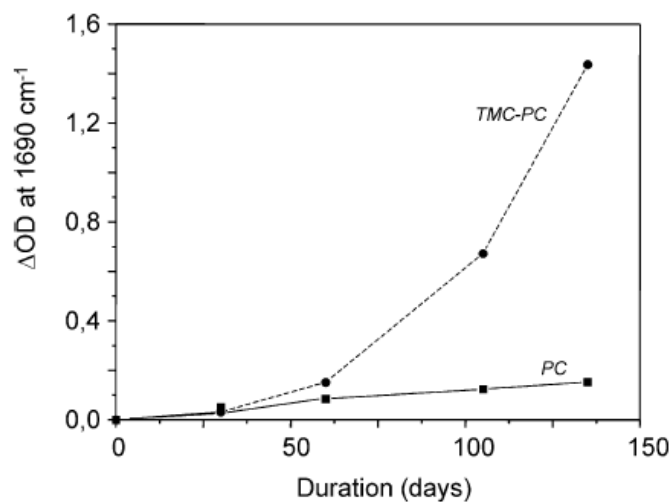


Fig. 20. Increase of the absorbance at 1690 cm^{-1} for thermo-oxidised PC and TMC-PC films as a function of thermo-oxidation duration at 170 °C.

Table 7
Changes in solubility determined by densimetry

Thermo-oxidation duration (days)	PC (%)	TMC-PC (%)
0	100	100
30	94	98
60	93	98
90	90	98

Table 8
Changes in M_w determined by SEC

Thermo-oxidation duration (days)	PC	TMC-PC
0	50175	65684
30	47818	59838
60	35589	49887
90	32242	46358

Macroradicals may also react separately by hydrogen abstraction on the aliphatic moieties of the polymer. The various resulting products identified as L_3 are formed in fairly low concentration and observed by IR spectrometry in the hydroxyl region (3607 , 3547 , 3470 cm^{-1}); these species or the products resulting from their photolysis are largely responsible for the yellow discoloration of polycarbonate films under non-oxidative conditions.

The concentration of L_3 species is observed to be higher in TMC-PC than in PC at the expense of L_2 . This can be attributed to the lower mobility and to the steric effect caused by the trimethylcyclohexylidene structure. Moreover, the presence of tertiary carbons in TMC-PC favors hydrogen abstraction by macroradical attack.

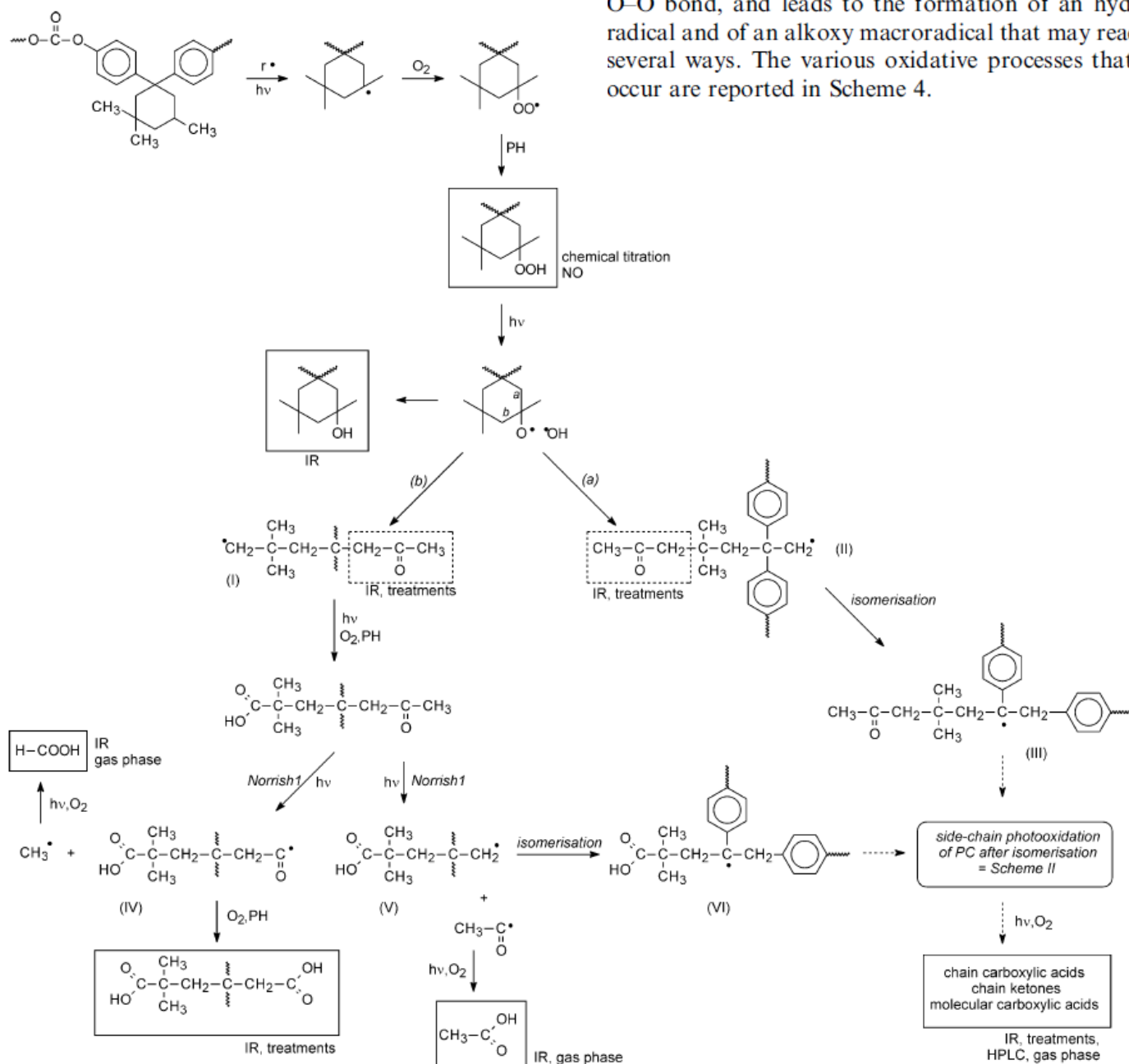
Under irradiation in the presence of oxygen, primary macroradicals are formed upon direct homolysis of the carbonate bond and are able to abstract the labile hydrogen atoms of the aliphatic units. They act as initiators of the oxidative phase of the photodegradation. L_1 , which absorbs directly the incident light $\lambda > 300\text{ nm}$, has been proposed to be a good candidate for the initiation of the long wavelength photo-oxidation of the aliphatic moieties of PC [2–5]. The initial step of the photo-oxidation of TMC-PC also involves the formation of L_1 (1689 cm^{-1} , 320 nm).

Hydrogen abstraction is generally considered as the first step in the mechanism of photo-oxidation of polymers. Two potential sites of abstraction exist on TMC-PC chains that contains tertiary and secondary carbon atoms. It is known that the tendency for hydrogen abstraction decreases from tertiary to primary carbon. The oxidation at the tertiary sites leads preferentially to chain breaking, while the oxidation at the secondary and primary carbons gives chain products without the scission of the backbone [16]. It has been shown that most of the photoproducts formed in the photo-oxidation of TMC-PC are low molecular weight or oligomeric species that can be extracted by methanol. It is therefore concluded that hydrogen abstraction occurs more easily at the tertiary carbon atoms of the trimethylcyclohexylidene units rather than at the secondary one.

Hydrogen atoms on the tertiary carbon of trimethylcyclohexylidene units are considerably more labile than those on the primary carbon of isopropylidene units. As a consequence, the reaction of oxidation of the trimethylcyclohexylidene units is easier than that of the isopropylidene units.

Once formed, the tertiary macroradicals react with oxygen to form peroxy radicals. Abstraction of a hydrogen atom to the macromolecular chain by the peroxy radicals leads to the formation of tertiary hydroperoxydes. The NO treatments of oxidised TMC-PC films showed that tertiary hydroperoxydes were formed. No secondary hydroperoxyde were detected. The concentration of hydroperoxide groups is higher in TMC-PC than that in PC. This confirms that hydrogen abstraction is enhanced on the tertiary carbon atoms of the trimethylcyclohexylidene units. The hydroperoxide values tend toward a plateau of ca. 50 mmol kg⁻¹ in TMC-PC and 10 mmol kg⁻¹ in PC (iodometric titration). This results from the photoinstability of hydroperoxydes groups, as already shown to be in the case of PC [2]. In the hydroxyl range of TMC-PC samples, the contribution of the hydroperoxydes to the absorption centred at 3470 cm⁻¹ has been calculated to be close to 25% after 150 h exposure using $\epsilon = 75 \text{ L mol}^{-1} \text{ cm}^{-1}$ for $\nu(\text{O-H})$ vibration.

The decomposition of hydroperoxides either by photolysis or by thermolysis involves the homolysis of the O-O bond, and leads to the formation of an hydroxy radical and of an alkoxy macroradical that may react by several ways. The various oxidative processes that can occur are reported in Scheme 4.



Scheme 4. Photo-induced oxidation of TMC-PC.

By abstraction of an hydrogen atom to the polymeric backbone, hydroxyl groups are formed. These hydroxyl groups contribute for about 75% to the development of the IR absorption centered at 3470 cm^{-1} (intermolecularly bonded OH groups of alcohols).

Another route of decomposition of the macroalkoxy radical is a β -scission. The two types of scission (a) or (b) imply the opening of the aliphatic ring, leading to the formation of end-groups aliphatic ketones, that correspond to the residual band at 1724 cm^{-1} observed in photo-oxidised films after SF_4 , MeOH or thermal treatments. β -Scissions generate primary radical (I) and (II).

The primary radical (I) $\bullet\text{CH}_2\text{-R}$ obtained in this reaction may decompose by an oxidation leading to primary hydroperoxides. The primary hydroperoxides are photochemically and thermally unstable and can be decomposed to give carboxylic acids by a direct oxidation or an oxidation involving the formation of aldehydes further oxidised into carboxylic acids.

Under exposure, a Norrish type I reaction of the end-group ketone occurs. Two routes of decomposition of the ketone can be proposed:

- formation of a methyl radical which is further oxidised into molecular formic acid; it can migrate out of the polymer matrix and it has been detected by analysis of the gas phase. The macroradical (IV) formed simultaneously is further oxidised into end-chain acids (observed at 1713 cm^{-1} and evidenced by SF_4 and NH_3 derivatisation);
- formation of an acetyl radical, which is further oxidised into acetic acid (that can migrate in the gas phase) and accompanied by the formation of a primary methylene macroradical (V).

As proposed for PC, isomerisation of the primary radical (V) occurs and leads to the formation of more stable tertiary benzylic radical (VI).

In the same way, isomerisation of the primary methylene radical (II) occurs to yield the tertiary benzylic radical (III).

The presence of aromatic acids (1696 cm^{-1}) and ketones (1690 cm^{-1}), as revealed by derivatisation treatments of oxidised TMC-PC films and the identification of benzoic acid, 4-hydroxybenzoic acid, hydroquinone and phenol, after methanolic extraction and HPLC analysis, confirm the isomerisation of the methylene radical as proposed in PC photo-oxidation.

The photo-oxidation of benzylic radicals (III) and (VI) involves an analogous mechanism as the one reported in Scheme 2 for the methylene macroradicals converted into tertiary benzylic radicals.

As a consequence, the same types of oxidation products are formed in PC and TMC-PC namely: chain carboxylic acids (1713 cm^{-1}), chain ketones (aliphatic at 1724 and aromatic at 1690 cm^{-1}) and molecular carboxylic acids (gas phase).

As proposed in the case of PC, the oxidation of aromatic rings of TMC-PC occurs under exposure. The dicarboxylic acidic products (1713 cm^{-1}) formed by ring opening can be thermally transformed in cyclic anhydride observed at 1860 and 1840 cm^{-1} .

1724 and aromatic at 1690 cm^{-1}) and molecular carboxylic acids (gas phase).

As proposed in the case of PC, the oxidation of aromatic rings of TMC-PC occurs under exposure. The dicarboxylic acidic products (1713 cm^{-1}) formed by ring opening can be thermally transformed in cyclic anhydride observed at 1860 and 1840 cm^{-1} .

Acid groups participate for 25% to the development of the IR absorption at 3330 cm^{-1} . This contribution is deduced from the thermolysis experiments of the samples pre-photo-oxidised at $\lambda > 300\text{ nm}$. Thermolysis provokes the migration of the low molecular weight species in the gas phase or the cyclisation of the dicarboxylic species into anhydrides.

Except for the nature of the macroradicals that initiate the oxidation by abstraction of hydrogen on the polymeric backbone, the same type of conventional radical mechanism, involving the formation of hydroperoxydes on aliphatic sequences, is proposed to account for the thermo-oxidation of PC and TMC-PC.

As observed in long wavelengths photo-oxidation, thermo-oxidation leads to the formation of two types of chain ketones: aliphatic at 1724 cm^{-1} and aromatic at 1690 cm^{-1} .

Ketones accumulate in thermo-oxidised films since Norrish type I reactions do not occur in thermal ageing. Dicarboxylic acids formed in ring oxidation thermally cyclise to form anhydrides observed at 1860 and 1840 cm^{-1} . For these two reasons, acid groups do not accumulate in thermo-oxidised films (as observed by IR analysis associated with derivatisation reactions). The absence of acidic species in thermo-oxidised films constitutes one of the most noticeable difference between thermo- and photo-ageing.

For the same reason, as observed in photo-oxidation, the thermal degradation of TMC-PC is easier than that of PC.

8. Conclusion

Hydroperoxides titration, physical and derivatisation treatments confirm the results deduced from the analysis of the UV and IR spectra: the trimethylcyclohexylidene units appear to be the source of much more oxidation than the isopropylidene units. The same trend is measured in photo-oxidation and thermo-oxidation ageing, in spite of the fact that TMC-PC has been synthesised to improve the heat resistance of PC. The higher oxidisability of TMPC is shown to result from the presence of labile hydrogen atoms on the tertiary carbon of the trimethylcyclohexylidene units.

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