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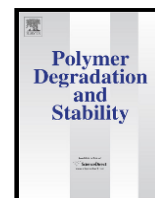
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Influence of chemical structural defects on the photostability of low-density polyethylene

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ABSTRACT

The photooxidation of four different polyethylenes with various amounts of chemical defects was examined. These polyethylenes had different initial contents of vinyl and vinylidene groups, and two of them exhibited an infrared absorption band attributed to ketones. The rates of photooxidation of these four polymers were rather different, and the rates of photooxidation increased with the initial concentration of ketones. The ketones were tentatively attributed to the use of propanal as a transfer agent during polymer synthesis and were readily eliminated by photolysis (irradiation in vacuum) of the samples. The identification of butanone formed by Norrish-II reactions confirmed the presence of propanal. Notably, the four samples behaved similarly after prephotolysis and degraded at the same rate. Moreover, the rates of photooxidation after prephotolysis were found to be totally independent of the concentrations of unsaturations, which does not confirm the hypothesis of a potential influence of such groups on the initial photostability of polyethylene.

1. Introduction

The role of chemical structural defects in the photooxidation of polymers in general, particularly polyethylene (PE), is of major importance for understanding the mechanism and kinetics of oxidation and remains a controversial question. These chemical defects have various structures, with unsaturations, hydroperoxides, and ketones being the most cited [1,2,3,4,5,6,7,8]. An abundance of existing literature has been devoted to the roles played by these different structures, but which defects are responsible for the initiation of photooxidation is unclear [9]. It has also been suggested that initiation could be attributed to charge-transfer complexes with O₂, in which oxygen is converted into water and alkyl radicals [10].

Chakraborty et al. [3] suggested that carbonyl initiation is only important in heavily oxidized polymers in the later stages of photooxidation. Amin et al. [11] found that when the carbonyl concentration is low, hydroperoxides and vinylidene are the main sources of photoinitiation. In the 1980s, Arnaud et al. [4] reported that the preferred oxidation site was a carbon at the α -position of vinylidene, suggesting that the vinylidene pathway is an important route of photooxidation. In contrast with Chakraborty et al. [3], it was found that the hydroperoxides formed during the thermal oxidation of PE films essentially do not initi-

ate subsequent photooxidation and thus have poor photoinductive ability. Hydroperoxides form a secondary cage structure that decomposes directly into ketones and water [12], and no radicals are formed. This last point has been independently confirmed several times [13].

It is known that polyethylenes of different origins degrade at different rates when exposed to environmental conditions, but no clear information has been given to explain the observed differences. It is usually considered that the unsaturations come into play and the more vinylidene is present, the more photooxidable a polyethylene is [4]. The chain structural defects in LDPE, which depend on the polymerization chemistry and processing conditions, include vinyl, vinylene and vinylidene double bonds—easily identified by infrared spectroscopy—together with short- and long-chain branches, hydroperoxides, and ketones. Measuring the concentration of unsaturations has been used as a criterion to facilitate the prediction of the intrinsic photostability of a given polyethylene. However, this is certainly not the only criterion to be considered, and in the current manuscript, we will consider results obtained using different LDPE with various levels of chemical defects exposed to photooxidation under accelerated conditions.

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2. Materials and experimentation

2.1. Polyethylene grades

Four low-density polyethylene grades (LDPEs) were used: Riblene® FC40F (denoted as PE-A) and Lupolen® 2420D (PE-B), respectively from Versalis and Basell, were produced by a tubular reactor process; Riblene® FC20 (PE-C) and Alcludia® PE-033 (PE-D), respectively from Versalis and Repsol, were produced via an autoclave process (Table 1).

2.2. Preparation of polymer films

Raw LDPE films with a thickness of 150 μm were obtained from blown extrusion at 200 °C on a single layer laboratory extruder at Barbier Group.

2.3. Photothermal ageing

The samples were irradiated in a SEPAP MHE unit (Atlas/Ametek) at 60 °C [14]. Three films for each formulation were exposed and characterized to ensure the reproducibility of the experiments. The SEPAP MHE was equipped with a medium-pressure mercury lamp (1000 W) located in the centre of the apparatus, around which the samples were placed on a rotating carousel. Wavelengths below 300 nm were filtered out. The irradiance between 300 and 420 nm was fixed at 90 $\text{W}\cdot\text{m}^{-2}$ ("M" mode). Irradiance and black standard temperature (T_{BST}) (fixed at 70 °C) were on-rack controlled by a wireless XENOSENSIV light sensor and a BST monitor, respectively. The temperature of the air in the device (T_{ch}) was controlled by a sensor placed inside the chamber and was regulated at 60 °C. As the polymer films used in this study were transparent, the temperature of the films was considered equal to the chamber temperature T_{ch} .

Table 1

Characteristics of the four LDPE samples used (commercial name and producer, synthesis process, melt flow index [MFI] and density).

Sample	PE-A	PE-B	PE-C	PE-D
Commercial name (producer)	Riblene® FC 40 F (Versalis)	Lupolen 2420 D (LyondellBasell)	Riblene® FC 20 (Versalis)	Alcludia® PE-033 (Repsol)
Synthesis process	Tubular reactor	Tubular reactor	Autoclave	Autoclave
MFI (190 °C/2.16 kg)	0.3	0.25	0.25	0.3
Density ($\text{g}\cdot\text{cm}^{-3}$)	0.928	0.923	0.922	0.921

2.4. Irradiation under vacuum (photolysis)

Photolysis experiments were performed on films introduced into borosilicate tubes sealed under a vacuum of 10^{-3} Pa obtained using a diffusion vacuum line. The tubes were then irradiated in the SEPAP MHE device for 200 h.

2.5. Soxhlet extraction

Soxhlet extractions were performed in methanol for 48 h. The films were then dried at ambient temperature for more than one week.

2.6. Characterization methods

The thickness of the samples (150 μm) was low enough to allow chemical changes to be monitored by infrared spectroscopy in transmission mode. The spectra were recorded with a Nicolet 6700 FTIR spectrometer (32 scans, 2 cm^{-1} resolution) working with OMNIC software. The very slight differences in film thickness were corrected using the absorbance at 1378 cm^{-1} as a reference. To plot the oxidation kinetics, the differences in the absorbance ΔA (1713 cm^{-1}) with respect to t_0 were measured.

The composition of the gas phase produced by the photolysis of PE was determined using headspace gas chromatography coupled with mass spectrometry (HS-GC/MS; Shimadzu HS-20 coupled with QP2010SE). The mass spectrometer source was heated to 200 °C, and identification of the major constituents was carried out using the NIST database.

3. Results and discussion

3.1. Characterization of the LDPE samples before irradiation

The initial content of vinyl ($\text{H}_2\text{C}=\text{CHR}$) and vinylidene ($\text{H}_2\text{C}=\text{CR}_2$) groups was determined by FTIR spectroscopy (see Fig. 1a) on the basis of the average molar extinction coefficients of model compounds such as hexenes, heptenes, and octenes: 122 $\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$ for vinyls (909 cm^{-1}) and 158 $\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$ for vinylidenes (888 cm^{-1}) [4]. The content of vinylenes ($\text{RCH}=\text{CHR}'$) in each PE sample was very low (the measured absorbances at 965 cm^{-1} were less than 0.005 for films of 150 μm thickness) and was not subsequently calculated. The values calculated for the vinylidene and vinyl contents are reported in Table 2.

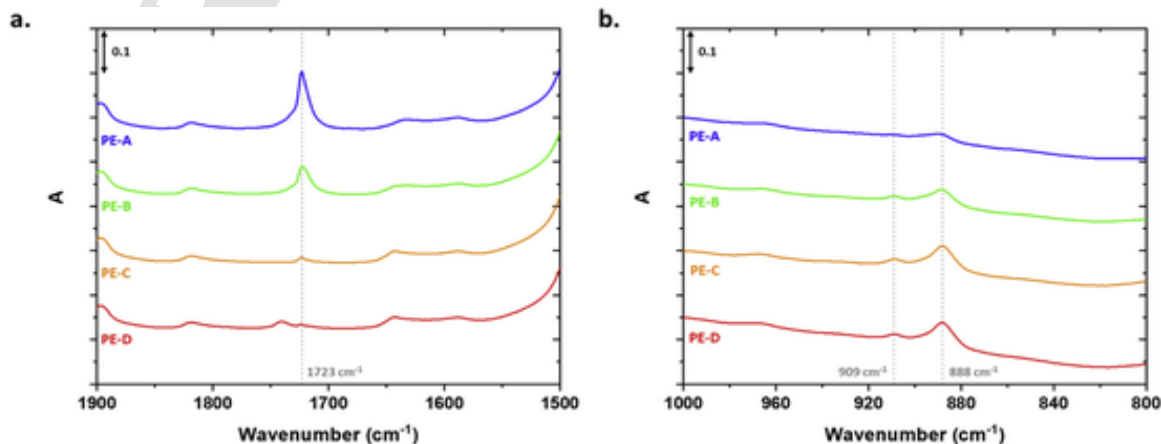


Fig. 1. Initial infrared spectra of the four LDPE samples (with a film thickness of 150 μm) in a. the carbonyl domain (1900–1500 cm^{-1}) and b. the unsaturations domain (1000–800 cm^{-1}).

Table 2

Initial absorbance at 909, 888 and 1723 cm^{-1} (with a film thickness of 150 μm) and corresponding initial concentrations of vinylidene, vinyl and ketone groups, respectively, for the four LDPE samples.

Sample	A(909 cm^{-1})	Vinyl (mol.L ⁻¹) =CHR	A(888 cm^{-1})	Vinylidene (mol.L ⁻¹) =CR ₂	A (1723 cm^{-1})	Ketone (mol.L ⁻¹)
PE-A	0.007	0.38×10^{-2}	0.019	0.79×10^{-2}	0.130	2.44×10^{-2}
PE-B	0.016	0.87×10^{-2}	0.039	1.65×10^{-2}	0.056	1.07×10^{-2}
PE-C	0.019	1.02×10^{-2}	0.055	2.29×10^{-2}	0.009	0.17×10^{-2}
PE-D	0.018	0.98×10^{-2}	0.054	2.26×10^{-2}	0.005	0.09×10^{-2}

As observed in Fig. 1b, the infrared spectra of the four LDPE samples also showed an absorption band at 1723 cm^{-1} , for which intensity varied between 0.005 and 0.130 (see Table 2). This frequency strongly suggests the presence of end-chain ketones[15,16] which, as discussed later in the manuscript, could result from the use of propanal as a transfer agent during the synthesis of PE[17]. Notably, this band was more intense for the two LDPE samples obtained by the tubular reactor process (FC40F and 2420D). The concentration of the carbonyl functional group at 1723 cm^{-1} was calculated using a molar absorption coefficient equal to 350 $\text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ for ketones[18] (Table 2).

3.2. Photooxidation of the LDPE samples

The modifications of the LDPE infrared spectrum during photooxidation have been reported many times and are well described in the literature[15]. The changes in the spectrum indicate the formation of ketones, carboxylic acids, esters and lactones, and the absorption bands of these photoproducts are convoluted in a broad absorption band with a maximum at 1713 cm^{-1} . The formation of isolated double bonds is also observed at 1640 cm^{-1} . Moreover, vinylenes and vinyl unsaturations are formed during photooxidative processes. No vinylidene unsaturations were detected at 888 cm^{-1} . The rates of photooxidation of the four LDPE samples were compared by measuring the increase in absorbance at 1713 cm^{-1} with irradiation time (Fig. 1).

The results given in Fig. 2 clearly indicate that the photooxidation rate is not the same for the different PE samples. It follows the order $A > B > C = D$. Compared with the initial concentration of structural defects given in Table 2 (vinyl and vinylidene groups, ketones), this order is consistent with the ketone content. In contrast, the ranking of photooxidation rates is opposite to the amount of initial unsaturation. The shapes of the four curves shown in Fig. 2 are slightly different,

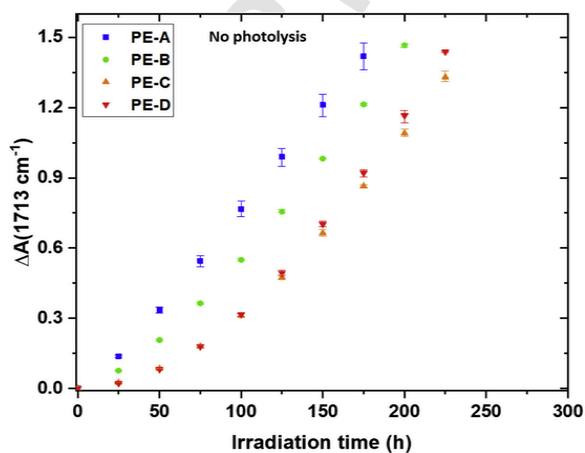


Fig. 2. Changes in absorbance at 1713 cm^{-1} (film thickness 150 μm) with irradiation time for the four LDPE samples exposed to artificial accelerated photooxidation (90 $\text{W} \cdot \text{m}^{-2}$, 60 $^{\circ}\text{C}$).

which suggests that there are at least two important processes in the kinetics. In the case of the more stable samples (PE-C and PE-D), the absorbance at 1713 cm^{-1} increases slowly in the first 100 h of irradiation and follows an exponential relationship, and after 100 h increases linearly. A similar behaviour is observed in the case of samples PE-C and PE-A (the less stable one), but the first phase with an exponential shape is limited to a short period and a linear increase of the absorbance is observed after approximately 50 h in the case of PE-B and only a few hours (around 25 h) in the case of PE-A.

3.3. Influence of the initial concentration of ketones on the photooxidation of the LDPE samples

The four kinetic curves are parallel after 100 h of irradiation and for that reason, the absorbance at 1713 cm^{-1} were compared for an irradiation time of 100 h and plotted as a function of the initial absorbance at 1723 cm^{-1} of the ketones (Fig. 3).

The results given in Fig. 3 suggest that the amount of photooxidation products is correlated with the initial concentration of ketones. It is well known that ketones can initiate photooxidation of LDPE since they absorb light in the UV domain of solar light. The band is weak and corresponds to the symmetry-forbidden $n\pi^*$ transition. The photocleavage of the carbon-carbon bond adjacent to the carbonyl group which arises from Norrish I reactions[19,20] produces radicals that initiate oxidation by hydrogen abstraction from macromolecular chains.

3.4. Influence of the initial concentration of unsaturation on the photooxidation of the LDPE samples

A similar correlation to that for ketones was tentatively applied to unsaturations. Fig. 4 shows the increase in the absorbance at 1713 cm^{-1} as a function of the initial absorbance at 909 (vinyls) and 888 (vinylidene) cm^{-1} .

Fig. 4 shows that, surprisingly, the rate of photooxidation decreases when the concentration of vinyls and vinylidenes increases. It seems that initial unsaturations do not initiate photooxidation of LDPE, which confirms previous results[13]. A first conclusion can be proposed considering the results presented in Figs. 3 to 5: the rate of photooxidation depends on the initial concentration of ketones, not on that of vinyls or vinylidenes.

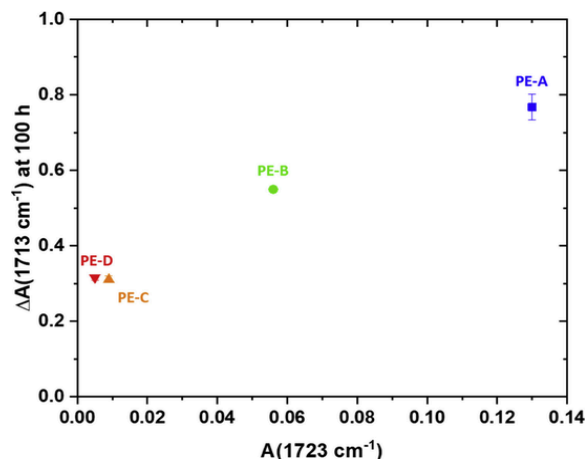


Fig. 3. Change in absorbance at 1713 cm^{-1} after 100 h of irradiation vs. initial absorbance at 1723 cm^{-1} for the four LDPE samples (film thickness 150 μm).

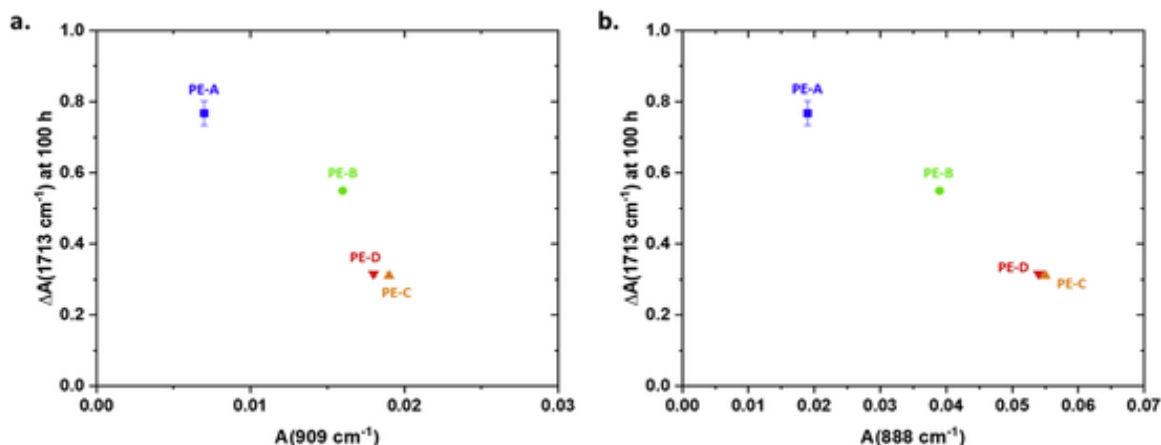


Fig. 4. Change in absorbance at 1713 cm^{-1} after 100 h of irradiation vs. initial absorbance at a. 909 cm^{-1} and b. 888 cm^{-1} for the four LDPE samples (film thickness $150 \mu\text{m}$).

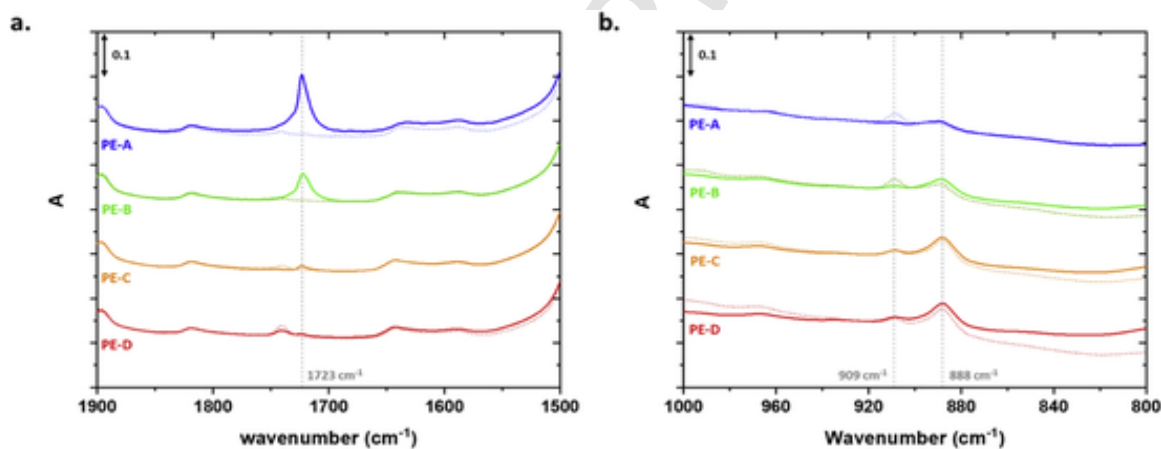


Fig. 5. Infrared spectra of the four LDPE samples (with a film thickness of $150 \mu\text{m}$) before (plain line) and after (dotted line) 200 h of photolysis in a. the carbonyl domain ($1900\text{--}1500 \text{ cm}^{-1}$) and b. the unsaturated domain ($1000\text{--}800 \text{ cm}^{-1}$).

3.5. Origin of the initial ketones

In this section, we report the results of irradiation under vacuum (photolysis) to monitor the fate of the ketones initially present in the PE samples. Before studying the effect of photolysis, the LDPE films were subjected to Soxhlet extraction in methanol, and the infrared spectra of the films before and after Soxhlet treatment were compared. The spectra were fully similar, which suggested that since ketones could not be extracted, they are linked to the macromolecular chains.

Fig. 5 shows the infrared spectra of the carbonyl and unsaturation domains before and after 200 h of light irradiation under vacuum (photolysis).

The spectra in Fig. 6 show that irradiation under vacuum led to the disappearance of the absorption band at 1723 cm^{-1} and provoked a slight increase in the band at 909 cm^{-1} (vinyls). No other modification of the infrared spectra was observed, in particular in the domain of the hydroxyl groups, which indicated that no detectable photoreduction occurred. Thermolysis at $100 \text{ }^\circ\text{C}$ for the same duration had no effect on the infrared spectra of the samples. The values of the absorbance at 1723 , 909 and 888 cm^{-1} after photolysis are given in Table 3.

The changes in the infrared spectra induced by irradiation under vacuum may be explained by the initial photolysis of the ketones at 1723 cm^{-1} . Two hypotheses were examined to explain the initial pres-

Table 3

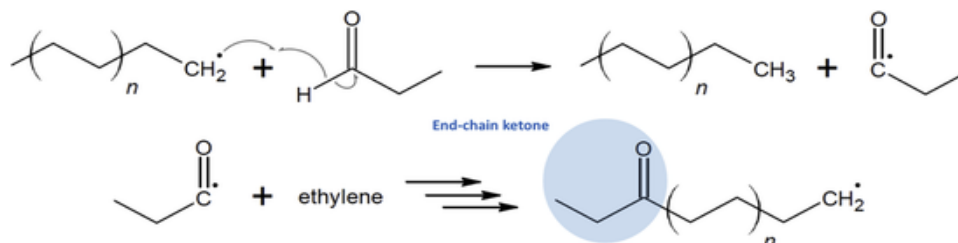
Absorbance at 1723 , 909 and 888 cm^{-1} after 200 h of photolysis for the four LDPE samples (values measured prior to photolysis are shown in brackets; see Table 1).

Sample	$A(1723 \text{ cm}^{-1})$	$A(909 \text{ cm}^{-1})$	$A(888 \text{ cm}^{-1})$
PE-A	0.002 (0.130)	0.032 (0.007)	0.016 (0.019)
PE-B	0.001 (0.056)	0.033 (0.016)	0.033 (0.039)
PE-C	0 (0.009)	0.022 (0.019)	0.055 (0.055)
PE-D	0.001 (0.005)	0.021 (0.018)	0.058 (0.054)

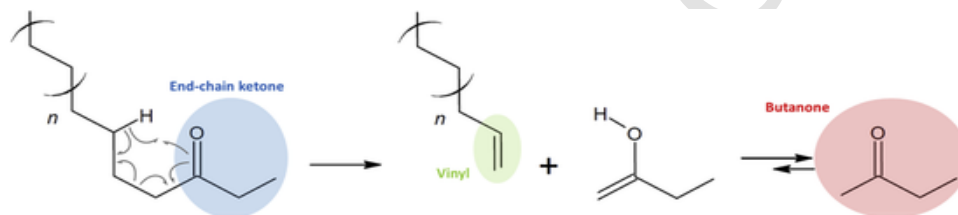
ence of the ketones. Ketones could have been formed by thermooxidation during processing of the samples. However, the infrared spectra shown in Fig. 6 are different from those acquired after thermal oxidation of LDPE[15]. The spectra in Fig. 6 did not show any evidence of other oxidation products that would also form during processing (acids, esters, etc.).

The second hypothesis involves the use of a transfer agent such as propanal during the synthesis of LDPE. By analogy with EVA copolymers[17], a transfer agent was very certainly used to reach the target molar mass range. This results in the formation of end-chain ketones, as shown in Scheme 1.

The Norrish type II reaction of the end-chain ketones, as presented in Scheme 2, may explain the changes in the spectra observed after pho-



Scheme 1. Proposed mechanism of radical transfer to propanal during LDPE synthesis.



Scheme 2. Norrish type II reaction applied to end-chain ketones.

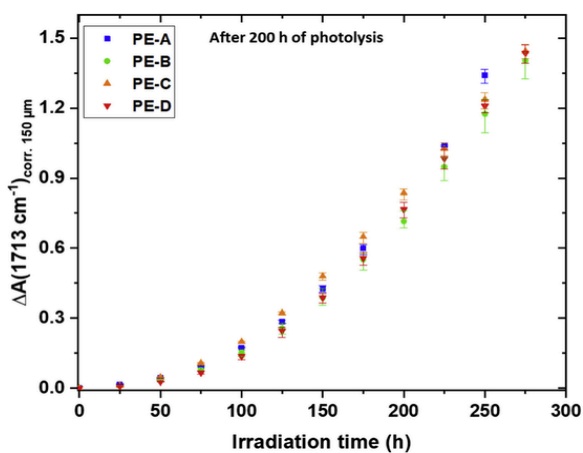


Fig. 6. Changes in absorbance at 1713 cm^{-1} with irradiation time for the four LDPE samples exposed to artificial accelerated photooxidation after 200 h of photolysis ($90\text{ W}\cdot\text{m}^{-2}$, $60\text{ }^\circ\text{C}$).

tolysis. The Norrish-II reaction involves the photochemical intramolecular abstraction of a γ -hydrogen to produce a vinyl group and an enol as the primary photoproducts[19]. The enol rapidly tautomerizes to butanone, which can be rapidly lost by migration and evaporation.

This photolysis reaction explains the modification of the infrared spectra presented in Fig. 5:

- Photolysis leads to a total loss of ketone absorption at 1723 cm^{-1} ;
- The vinyl concentration at 909 cm^{-1} increases.

The loss of butanone by evaporation should lead to a decrease in the mass of the sample after irradiation under vacuum. To measure the mass variation provoked by photolysis, a “large” film of PE-A (a few cm^2 with a thickness of $150\text{ }\mu\text{m}$) was placed in a borosilicate tube and sealed under vacuum. The tube containing the film was then irradiated for 200 h in the SEPAP MHE device, and the infrared spectrum of the film was recorded before and after irradiation. As expected, a decrease in the absorbance of 0.127 at 1723 cm^{-1} was measured, which corre-

sponded to a loss of $0.024\text{ mol}\cdot\text{L}^{-1}$ of butanone ($\epsilon_{1723\text{ cm}^{-1}} = 350\text{ mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$), which was equivalent to 0.025 mmol (the initial weight of the sample before photolysis was 0.9577 g). In parallel, a mass decrease of 0.0012 g was measured, which corresponded to a loss of 0.017 mmol of butanone (molar mass of butanone = $72\text{ g}\cdot\text{mol}^{-1}$). This value is on the same order of magnitude, and the results obtained by gravimetric and spectroscopic analysis are consistent (indicating that 0.017 and 0.025 mmol of butanone, respectively, were formed by the Norrish type II reaction).

A second set of experiments was performed to confirm the formation of butanone by the loss of ketones at 1723 cm^{-1} under photolysis conditions. A PE film was placed in a vial and irradiated in an argon atmosphere to avoid any oxidation. The gas phase was then collected with a syringe and analysed by mass spectrometry. The analysis clearly indicated the presence of a peak attributable to butanone. This fully confirmed the hypothesis of a Norrish-II reaction involving end-chain ketones, as described in Scheme 2.

3.6. Photolysis of ketones and impact on the photooxidation of the LDPE samples

In this section, we report on the impact of photolysis on subsequent photooxidation. This was done to monitor the influence of the ketones on the rate of photooxidation. After 200 h of photolysis, the LDPE samples were subjected to artificial accelerated ageing under photooxidation conditions as described above (see Fig. 2). The oxidation kinetics curves at 1713 cm^{-1} are shown in Fig. 6.

Fig. 6 shows that photolysis dramatically modified the photooxidation rate of the samples. A decrease in the photooxidation rate was observed, and this decrease was particularly important for the two samples that initially had the most substantial concentration of ketones at 1723 cm^{-1} .

Interestingly, the four kinetic curves are similar after photolysis, and unique behaviour can be observed for the four LDPE samples in terms of photooxidation rates. As an example, after 100 h of exposure, an absorbance of approximately 0.16 at 1713 cm^{-1} was reached. This point was reported in Fig. 4 above, and it confirms the curvature of the photooxidation rate when increasing the amount of absorbed light. The absorbance of 0.16 measured for $I_a/I_0 = 0$ is related to the rate of pho-

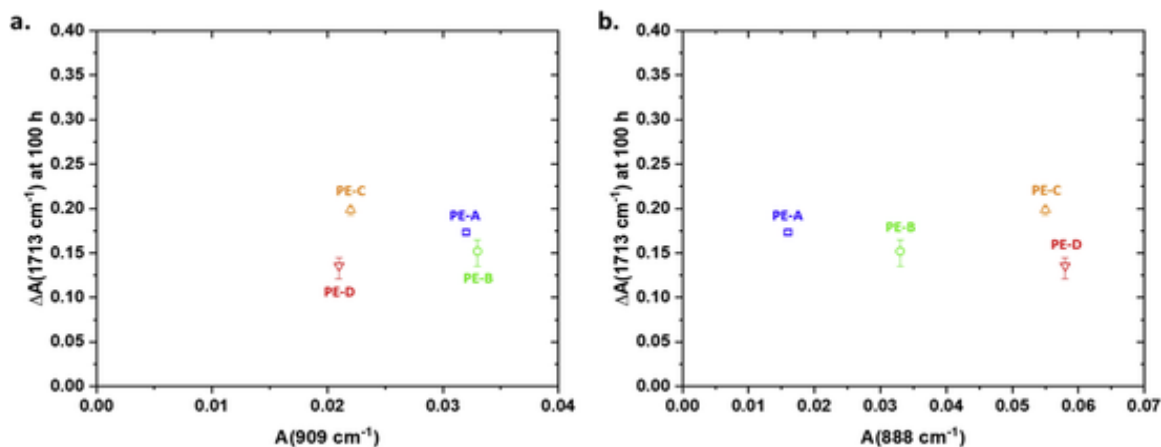


Fig. 7. Change in absorbance at 1713 cm⁻¹ after 100 h of irradiation vs. initial absorbance at a. 909 cm⁻¹ and b. 888 cm⁻¹ for the four LDPE samples after photolysis (film thickness 150 μm).

tooxidation caused by initiation, which does not involve the photodissociation of ketones.

The kinetic curves plotted in Fig. 7 clearly show that after photolysis:

- The rate of photooxidation decreases, which confirms that ketones play a dramatic role in the initiation of photooxidation. The disappearance of these compounds can reduce the photooxidation rate.
- After elimination of the ketones by preliminary photolysis, the rates of photooxidation of the four LDPE samples are similar, which means that in the absence of initiation by ketones, the various LDPE samples behave similarly in terms of their sensitivity to photooxidation. Moreover, plotting the rate of oxidation as a function of the concentration of vinylidenes (represented by the absorbance at 888 cm⁻¹), as shown in Fig. 7, indicates that the rate of photooxidation is almost constant and independent of the concentration of vinyls and vinylidenes.

4. Conclusion

A comparison of the photooxidation of four LDPE samples with different initial contents of unsaturations and ketones showed that the rate of photooxidation increased with the initial content of ketones. The ketones were identified as end-chain ketones resulting from the use of propanal as a transfer agent during synthesis. Ketones can be eliminated by photolysis (irradiation under vacuum), which leads to the formation of butanone and extra vinyl unsaturations by the Norrish-II reaction, as identified by MS and FTIR spectroscopy, respectively.

After photolysis, the rates of photooxidation were identical for the four LDPE samples and were independent of the concentration of unsaturation. It appears that after appropriate treatments, a unique kinetic curve can describe the photooxidation of LDPE of different origins, despite different initial amounts of chemical defects.

In conclusion, the photooxidation rate of low-density polyethylene does not depend on the concentration of vinyl, vinylene or vinylidene double bonds but strongly depends on the concentration of ketones that could initially be present in the polymer.

CRediT authorship contribution statement

Emma Mazeau: Investigation. Alexy Duchamp: Investigation. Gérard Pichon: Investigation. Bruno Bouchut: Validation. Julien Christmann: Writing – review & editing. Sandrine Therias: Writing

– review & editing, Supervision. Jean-Luc Gardette: Writing – review & editing, Writing – original draft, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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