Identification of Additives in Polypropylene and Their Degradation under Solar Exposure Studied by Gas Chromatography–Mass Spectrometry

Enrique Blázquez-Blázquez, María L. Cerrada, Rosario Benavente, and Ernesto Pérez* "

ABSTRACT: Additives are absolutely essential in the development of commercial polymeric materials. Accordingly, an exhaustive control of composition and evolution in these additives over time is necessary to validate their performance and safety during their shelf life and, consequently, their ultimate applications. Gas chromatography coupled with mass spectrometry, GC–MS, is described in the present work to identify and analyze the content of a wide variety of additives, commonly used in industrial polymeric materials. First, the identification under the present experimental protocol of additives with a relatively high molecular weight (Irganox 1330 and Irganox 1010) has been successfully attained. Second, the evolution under solar exposure over time has been analyzed by GC–MS for 11 additives and derived substances, which have been identified in a commercial polypropylene sample, estimating the corresponding depletion times. In addition, the resultant increase of carbonyl groups in the polymeric macrochains along the photo-oxidation has been also determined by infrared spectroscopy. Therefore, GC–MS is found to be a reliable tool for the analysis of the evolution of commonly used polymer additives under specific degradation conditions, which can be very useful in the formulation of improved future additivations.

1. INTRODUCTION

Polymers are currently one of the most commonly used materials. Among them, the complete hydrocarbons (polyethylene (PE), polypropylene (PP), polystyrene (PS)) together with poly(vinyl chloride) (PVC) represent the largest segment of industrial polymers. This fact explains why antioxidants, lubricants, and stabilizers comprise a large part of the organic additives since they are most frequently used in polymer formulations for protection against degradation during processing or during their environmental exposure to the action of oxygen and/or ultraviolet (UV) radiation.1–3

Thus, all types of commercial polymer-based materials, including thermoplastics, thermosets, and rubbers, require a correct additivation, essential for optimizing their ultimate properties and prolonging their useful life. Additives are often used in a dual role: on the one hand, to promote protection against external agents and, on the other hand, to contribute in the modification of the physical, chemical, and thermal properties of the final material.

Several works have been devoted to the evaluation of additives in polymers,4–10 but considering the relatively high molecular weight of some additives, many of those studies use high-performance liquid chromatography (HPLC) coupled with different types of detectors, i.e., mass spectrometry (MS) or UV. The simultaneous identification of unknown complex mixtures of additives and their degradation products is not, however, straightforward by HPLC since it requires an extra effort to make the decision on the appropriate and optimal ionization mode for each different additive.5

Gas chromatography–mass spectroscopy (GC–MS) has been also used as a fast and simple technique to determine additives in polymers,10–15 with an optimum chromatographic resolution power. GC–MS allows solving numerous industrial problems,16–19 namely, the nontargeted analysis (where the identification of additives or components of a mixture has to be performed), and also the migration of additives and the existence of residual monomers, which may be indicative of the quality of a specific product for its massive consumption.

One of the limitations of the GC–MS techniques is the analysis of substances with a relatively high molecular weight. Their evaluation can be, however, performed using shorter columns with phases as thin as 0.1 \( \mu \text{m} \).\textsuperscript{20,21} available for temperatures as high as 400 \( ^{\circ} \text{C} \).

The main groups of additives customarily used in polymer formulations that can be analyzed and quantified by the GC–MS technique are, among others, antioxidants, UV stabilizers and absorbers, thermal stabilizers, lubricants, plasticizers, and...
flame retardants. These additives are, thus, necessary for protecting the final material from degradation and/or boosting the improvement of its properties. For instance, they are of capital importance in polymer formulations for outdoor applications, as is the case of plastics in agriculture. In other cases, however, some additives, or their degradation products, may involve specific health safety problems, namely, in materials with applications for drinks and food packaging.

Studies dealing with various additives in different polymers have been reported, including PE, PP, PVC, poly(ethylene terephthalate),6,8,26 and also multilayer films.27 Practically all polymer formulations include specific additives, depending mainly on their precise final application.

The main objective of the present research is to propose the use of gas chromatography coupled to mass spectrometry (GC−MS) as an applicable and reliable approach for the assessment of some common additives incorporated routinely into polymers. The aim is twofold: first, the identification under the present experimental protocol of additives with a relatively high molecular weight has been tested. The second objective has been the study of the effect of photo-oxidation on a commercial sample of PP that has been exposed to natural climatic conditions. That analysis is carried out both in the polymer itself and in the different additives included in the sample. Thus, the relative variations of the distinct additives are determined as a function of solar exposure. Moreover, the formation of oxidized species in the polymeric macrochains along this environmental aging is examined by Fourier transform infrared (FTIR) spectroscopy. Additionally, the linear retention index (LRI) for commonly used additives and their degradation products is determined.

2. SOLAR EXPOSURE PROTOCOL

Pieces of the compression-molded sheets (see Section 5 at the end of the manuscript) were exposed to the actual weather environment under tests ASTM G 7-99, ASTM D 1435-99, and ASTM D 5272-92. The photo-oxidation was carried out during 57 days in the summer season. The weather conditions in this period and location were characterized by rather high temperatures (sometimes above 40 °C), with practically no cloudy days and very low relative humidity.

Figure 1 shows the intensity of solar energy to which the samples have been exposed. The dots indicate the days when samples were collected for analysis. It can be observed that there is a linear relationship between solar energy and time (up to around 45 days), with a final deviation from that linearity ascribed to being more at the end of the summer season.

3. RESULTS AND DISCUSSION

3.1. Analysis of High-Molecular-Weight Additives.

The first objective of this study has been the identification of additives with a relatively high molecular weight under the present experimental protocol. Two additives found in many polymeric formulations have been analyzed: Irganox 1330 (also named as Ethanox 330), with $M = 775$ g/mol, and Irganox 1010 ($M = 1178$ g/mol).

The results concluded the feasibility of detecting these two compounds. Thus, although it is not possible to detect the intact Irganox 1010 (since its high molecular weight prevents it from being volatilized at the working temperature of the injector), it is, however, recovered from the polymer by ordinary extraction protocols.

Then, its presence in a certain polymer can be easily deduced from the observation of its degradation products, and to get the most output of the GC−MS technique, we have systematized the degradation path of this compound. Thus, the injection of this intact additive in the chromatographic system allows observing a repetitive degradation pattern, which can be seen in Figure 2.

Figure 2. Chromatogram showing the degradation products of Irganox 1010.

It has to be considered that these compounds from Irganox 1010 are degradation products obtained in the injector, standing in contrast to the so-called nonintentionally added substances (NIASs), which are compounds formed during the regular processing and useful lifetime of the polymeric material.9,25

The assignment of the degradation products of Irganox 1010 appearing in Figure 2 has been carried out by considering their mass spectra (see the Supporting Information, Figure S1) and previously reported studies, which indicate that the hydrolysis of the ester bond is the predominant degradation mechanism.28 Those authors proposed the structures of several degrading products obtained under accelerated aging tests. In the present GC−MS conditions, at least seven different structures have been identified. Some of them have been described before;28 however, it is important to keep in mind that there were identified by HPLC.

The degradation pattern depicted in Figure 2 is, therefore, the key characteristic to discern the presence of Irganox 1010 in a particular sample. The most abundant degradation product corresponds to methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, Metilox. The tentative assignment of other
degradation substances is depicted in Scheme S1 of the Supporting Information.

Therefore, Irganox 1010, if present in a certain sample, should produce the degradation pattern shown in Figure 2, i.e., all of the degradation peaks have to be observed simultaneously and with the intrinsic relative areas deduced from that figure (as explained, Metilox can also arise from the degradation of Irganox 1076). Obviously, it can be argued that those compounds may have been originally present in the sample, either because they were added as additives or because they have been produced by a former degradation product during the processing or lifetime conditions of the material. The first possibility is highly improbable, since those compounds are not regular additives, and all of them have to appear with the fingerprint in Figure 2, for the particular column and experimental conditions employed. The second one is also improbable, considering that the degradation products in that figure have been obtained under the rather rigorous conditions of the injection system (see Section 5), with temperatures considerably higher than those employed in the regular processing of a polymer material.

Another additive of relatively high molecular weight is Irganox 1330, mentioned above. In this case, the intact antioxidant can be, however, detected by GC−MS, and the chromatogram corresponding to the original nondegraded Irganox 1330 can be observed in the upper part of Figure 3.

![Figure 3. Chromatograms of the original and degraded Irganox 1330.](image)

This additive can undergo degradation under processing or useful lifetime conditions; in such a case, the degraded substances are, therefore, NIAS. The middle chromatogram in Figure 3 shows the degradation compounds for a sample of Irganox 1330 that has been exposed at 250 °C for 40 min, corresponding to around 27% degradation. It can be observed that the intact Irganox 1330 is still the most abundant compound (peak at 34.0 min, LRI = 4870), and the three extra peaks arising from the NIAS are also observed (in fact, the original sample shows already a small amount of the degradation product appearing at 33.7 min).

The lower chromatogram in Figure 3 corresponds to a sample subjected to more severe degradation conditions (80 min at 250 °C), where the intact Irganox 1330 has practically disappeared (92% degradation), and now the most abundant compound is the one observed at 33.1 min.

The nature of these compounds produced from the degradation of Irganox 1330 and their mass spectra can be seen in the Supporting Information (Scheme S2 and Figure S2).

### 3.2. Degradation of Additives in Polypropylene under Solar Exposure

The second aim of this work has been the study by GC−MS of the evolution of different additives over time in a specific commercial PP sample that has been exposed to natural weathering conditions for different periods (see Figure 1 for the variation of the solar energy received by the samples). Figure 4 shows the chromatograms of the extracts corresponding to the initial sample (0 days) and to that after 57 days of solar exposure.

![Figure 4. Chromatograms of the extracts corresponding to the initial sample (0 days) and to that after 57 days of solar exposure.](image)

Of the extracts corresponding to the initial sample and to that with the maximum solar exposure analyzed (57 days). From these chromatograms, and from the corresponding mass spectra, 11 additives have been identified (plus the oxidized form of Irgafos 168, labeled as Irg168ox), as shown by the legends in Figure 4 for the chromatogram corresponding to day 0. Figure 4 also includes 4-cyano-4′-n-oxyoctyl-biphenyl, 8OCB, added to the different extracts as an internal standard.

A more detailed report is given in Table 1, where the name and CAS number, structure, retention time, molecular weight, and a linear retention index of the additives are presented. As observed, different antioxidants, UV stabilizers, plasticizers, and lubricants were detected.

A minor amount of Metilox is also observed. This compound is reported to be a degradation product of Irganox 1076 or Irganox 1010.2,7,12,13,15−29 Since there is no sign of other degradation products of Irganox 1010 (compared with Figure 2), this small amount of Metilox is supposed to arise from the degradation of Irganox 1076 present in the sample.

As mentioned in Section 5, the values of the apparent concentration of different additives were determined from the individual peak areas in relation to the area obtained for the internal standard, 8OCB. The corresponding variation with exposure time is shown in Figure 5. The natural variable is the solar energy received by the samples, but Figure 1 shows the relationship between that parameter and the time of exposure, which is more insightful. Anyway, it can be observed in Figure 5 that the maximum intensity corresponds to Irgafos 168, while the initial amount of Tinuvin 770 is the lowest for the additives found and analyzed.

Figure 5 shows that these relative concentrations cover a wide range (more than 2 orders of magnitude), and, in order to get a more intuitive picture of their variation with solar exposure, the percentages related to the initial concentration are represented in Figure 6.

It is important to point out that although the overall peaks in the chromatograms (like those in Figure 4) may be rather...
small and involve huge uncertainty, the relative variation of some additives has been evaluated (see Section 5) under SIM mode (selected ion monitoring) from the analysis of the more representative \( m/z \) peak in the corresponding mass spectrum.

Coming back to Figure 6, the relative variations of additives can be categorized into three groups. In the first one, corresponding only to bis(2-ethylhexyl) adipate, shows a practical constancy with exposure time, indicating that it does not exhibit significant degradation over the analyzed exposure. The reason may be the presence of less labile groups in this compound.

The second group (the more numerous one, which includes seven compounds) shows an “intermediate” rate of depletion. If the time necessary for 50% depletion, \( t_{0.5} \), is taken as a simple parameter, this group presents values for this parameter from around 15 to 40 days.

Finally, there is a third group with a much higher rate of depletion: less than 10 days for \( t_{0.5} \), including three additives: isopropyl myristate, erucamide, and Irgafos 168.

It follows, therefore, that under solar exposure most of these additives are considerably degraded and consumed, and it is important to mention that the depletion of these additives (with the exception of adipate) follows an exponential behavior, inside the experimental error. Thus, the time dependence of these processes can be expressed by an exponential function of the type

\[
I = I_0 \exp(-t/\tau)
\]

where \( I_0 \) and \( I \) are the initial concentration and that at time \( t \), respectively, and \( \tau \) is the characteristic time of depletion so that \( 1/\tau \) represents a kind of rate for the degradation process. Obviously, the time for 50% depletion, \( t_{0.5} \), mentioned above, corresponds to \( I/I_0 = 0.5 \), so that from eq 1 it follows that \( \tau = \)

| Name (CAS no.) | Structure | \( t_R \) (min) | \( M \) | LRI |
|----------------|-----------|---------------|-----|-----|
| BHT-Aldehyde (1620-98-0) | | 9.40 | 234 | 1750 |
| Isopropyl Myristate (110-27-0) | | 10.32 | 270 | 1825 |
| 7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione (82304-66-3) | | 11.31 | 276 | 1905 |
| Tributyl aconitate (7568-58-3) | | 14.22 | 342 | 2160 |
| Acetyl tributyl citrate, ATBC (77-90-7) | | 15.30 | 402 | 2265 |
| Oleamide (301-02-0) | | 16.11 | 281 | 2345 |
| Bis(2-ethylhexyl) adipate (103-23-1) | | 16.56 | 370 | 2390 |
| Erucamide (112-84-5) | | 20.00 | 337 | 2770 |
| Tinuvin 770 (52829-07-9) | | 22.61 | 480 | 3090 |
| Irgafos 168 (31570-04-4) | | 25.10 | 647 | 3430 |
| Irganox 1076 (2082-79-3) | | 26.27 | 530 | 3600 |
| Irgafos 168 oxide (95906-11-9) | | 26.33 | 662 | 3610 |
Therefore, either $\tau$ or $t_{0.5}$ can be used for characterizing the process, although $t_{0.5}$ is slightly more intuitive.

Figure 7 shows the values of time $\tau_{0.5}$ for different additives. Irgafos 168 presents the highest degradation rate, as deduced from this figure; precisely, its own degradation is supposed to protect the entire system (polymer and also the other additives).30,31 Regarding this additive, it is important to mention that its decomposition involves the formation of an oxidized form (structure represented in the last file of Table 1). The concentration of Irgafos 168 in the extract for the highest solar exposure is diminished very much (see upper chromatogram in Figure 4), with the corresponding increase of the signal for the oxidized form of Irgafos 168. However, the initial chromatogram shows also a very important proportion of oxidized Irgafos 168. In fact, the corresponding quantification gives a value of around 40% in the oxidized structure for the day labeled as 0. It means that a considerable degradation has occurred prior to these experiments (including the initial petilization of the polymer, its posterior exposure to ambient conditions, and the compression-molding into sheets for these analyses). That percentage of 40% means that the initial state corresponds to around 5 days of solar exposure when considering the results in Figure 6.

It is important to consider that the relevance of the observed degradation rates will depend mainly on the purpose intended for a particular additive. Thus, certain additives may be used only as lubricants for facilitating polymer processing, so it does not matter if that additive degrades more rapidly. The opposite case corresponds to antioxidants, where it is essential that they last as much as possible in the polymer system. In Figure 7, we focus our attention on the additives with the fastest degradation rates isopropyl myristate, erucamide, and Irgafos 168; among these, the first two are lubricants, mostly intended for processing, so that their formulations may be appropriate. In the case of Irgafos 168, however, a more convenient formulation has about twice the initial concentration found in the studied polymer sample.

The effect of photo-oxidation in the PP sample itself has also been studied by monitoring the evolution of carbonyl groups. This analysis has been performed by FTIR-attenuated total reflectance (ATR) both in the initial polymer and in the samples after solar exposure. Additionally, a small amount of polymer without additives (they were extracted as detailed in Experimental Section) has been also exposed to solar irradiation (up to 29 days).

It has to be considered that only when the concentration of antioxidants has been reduced very much, then the polymer begins to degrade appreciably.14 The results in the carbonyl region (plus those associated with the band at 1460 cm$^{-1}$ taken as reference) are displayed in Figure 8 for some selected samples (with and without additives). The band at 1460 cm$^{-1}$ is ascribed to the asymmetric deformation vibration of the methylene group, as an internal standard.32,33 It can be clearly observed in Figure 8 that the original PP sample exhibits already a small number of carbonyl groups, mainly centered at 1735 cm$^{-1}$, attributed to ester groups,34-37 with a much smaller proportion of the band at 1712 cm$^{-1}$, assigned to acid groups.34,36-39 The total amount of carbonyl groups rises with solar exposure, and this increase is considerably higher, as expected, for the PP sample without additives. Moreover, there is a clear inversion of the relative intensities between the bands at 1735 (ester groups) and 1712 cm$^{-1}$ (acid groups), so that the latter species become dominant at high exposure times. A third component of the oxidation species appears at 1780 cm$^{-1}$, attributed to lactones.36,37,40 This behavior differs somewhat from those of other findings,36 where initially the band at 1712 cm$^{-1}$ is dominant and the band at 1735 cm$^{-1}$ becomes dominant only after more
than 80 h of thermo-oxidation. Moreover, the relative proportion of lactones (band at 1780 cm\(^{-1}\)) is much more relevant in that work. This trend was also found in isotactic metallocene iPP irradiated by different doses of the electron beam.\(^{41}\) It should be indicated, however, that the additivated of those PP samples is rather different from that in the present case. Furthermore, the electron beam irradiated specimens were synthesized with a metallocene catalyst instead of using a Ziegler–Natta one and, consequently, important microstructural variations exist.\(^{41}\) It has to be considered that the amount of thermo-oxidation, in addition to the presence of stabilizers, depends on details of both chemical and physical structures of the polymer.\(^{42}\)

Quantification of the carbonyl groups has been made by integrating all of the signals involved in this region, from 1640 to 1820 cm\(^{-1}\), considering that the carbonyl species include those various components and that their relative intensity changes considerably with oxidation degree. The results are shown in Figure 9.

As expected, the amount of carbonyl groups in the nonadditivated sample is considerably higher, by a factor of around 5, than that found in the sample with additives. A rather similar value has been reported before,\(^{43}\) where the factor between nonadditivated and additivated PP sample was around 6. The difference observed with the present results is that a certain induction period took place before a significant amount of carbonyl species were detected in the aforementioned study\(^{43}\) and in other works.\(^{38}\) Here, the results in Figure 9 show a continuous increase of the carbonyl signals, without the “induction” period. The reason might be associated with the fact, mentioned above, that the initial PP sample previous to its solar exposure already shows a significant amount of the oxidized form of Irgafos 168, corresponding to about 5 days of irradiation.

An important feature is the evolution of the two main components of the carbonyl signal. The component at 1735 cm\(^{-1}\) (related to ester groups) is dominant in the initial stages of the photo-oxidation, as observed in Figure 8. The rate of formation of species appearing at 1712 cm\(^{-1}\) (acid groups) is, however, considerably higher than that related to the band at 1735 cm\(^{-1}\) (by a factor of around 1.5 in both additivated and nonadditivated samples). This is the reason why the component at 1712 cm\(^{-1}\) becomes dominant at high exposure times.

As a final aspect, the effect of photo-oxidation is clearly noticed from the progressive whitening of the samples (see Figure S3 in the Supporting Information).

4. CONCLUSIONS

Gas chromatography coupled with mass spectrometry, GC–MS, has been proved to identify and analyze the content of a wide variety of common additives used in polymeric materials (antioxidants, UV stabilizers, lubricants, plasticizers), including the evaluation of additives with relatively high molecular weights and their degradation compounds.

Thus, the identification under the present experimental protocol has been successfully attained in the case of two additives of relatively high molecular weights found in many polymeric formulations: Irganox 1330 (also named as Ethanoi 330), with \(M = 775\) g/mol, and Irganox 1010 (\(M = 1178\) g/mol).

Moreover, GC–MS has been also effectively tested for analyzing the evolution of 11 additives identified in a commercial PP sample as a function of solar exposure time, and the corresponding depletion times have been determined.

The effect of photo-oxidation in the PP sample itself, studied by FTIR–ATR, indicates that the amount of carbonyl groups in the sample with additives is, as expected, considerably lower, by a factor of around 5, than that found in a nonadditivated sample.

There is also a clear inversion of the relative intensities between the bands at 1735 cm\(^{-1}\) (ester groups) and 1712 cm\(^{-1}\) (acid groups). The latter species become dominant at high exposure times since their rate of formation is higher than that for the ester groups by a factor of around 1.5.

In conclusion, GC–MS under the present experimental protocol is found to be a powerful and reliable tool for the analysis of the commonly used polymer additives and their evolution under specific degradation conditions, which can be very useful in the formulation of improved future additivations.

5. EXPERIMENTAL SECTION

A commercial Ziegler–Natta isotactic PP has been used for this study, with the following characteristics: melt flow index of 4.2 g/min (at 230 °C, load 2.16 kg); \(M_w = 395\) 000 g/mol; \(M_w/M_n = 6.5\); melting temperature: 161 °C. This particular polymer is intended for use under weathering conditions.
Sheets around 500 μm thick were obtained by compression molding in a Collin press at 210 °C for 4 min and at a nominal pressure of 25 bar, followed by slow cooling to room temperature at the same pressure.

The samples were exposed to the actual weather environment for 57 days in the summer season (see Section 2). For this purpose, a self-made aluminum sample rack was used, placed on the roof of our institute located in Madrid (coordinates 40°25′ N, 3°41′ W). As recommended by the standard, the rack is positioned with an inclination of 45° on the horizontal base, oriented toward the south, and at more than 1 m above ground level. The amount of solar energy was measured using a KIMP and ZONEN radiometer model Solarimeter Integrator CC2 located next to the sample rack. This equipment measures the accumulated solar energy between 300 and 3000 nm.

The evolution of additives was analyzed periodically, taking the solar energy received as a variable. These samples were extracted in a Soxhlet with dichloromethane for 8 h by taking 1.2 g of each exposed sheet and using 70 mL of organic solvent. Once the programmed extraction period was finished, the solvent was concentrated in a rotary evaporator. The stable at high temperatures, and it is not present in polymer samples. The 8OCB is one of the components of the well-High capillary column (15 m length Packard 6890 GC gas chromatograph equipped with an electron impact (70 eV) was the selected type of ionization for the mass spectrometer.

The analytical determination was carried out using a Hewlett Packard 6890 GC gas chromatograph equipped with an Agilent Technologies mass spectrometry detector model 5973. The separation of the compounds was performed on a DB5-HT capillary column (15 m length × 250 μm internal diameter and 0.1 μm film thickness). The carrier gas used was helium with a flow rate of 1 mL/min. A volume of 1 μL of the obtained extract was injected in split mode with a split ratio of 20:1, at 270 °C. An Agilent glass liner, containing glass wool, was employed.

The chosen chromatographic method lasted 37.5 min. The initial test temperature was 80 °C, which was increased up to 340 °C at a controlled rate of 8 °C/min. It was maintained at that temperature for 5 min. This method is suitable for optimum separation of a wide range of compounds found frequently in polymers, and also of linear hydrocarbons between around C12 (dodecane) and C49 (nonatetracontane). The electron impact (70 eV) was the selected type of ionization for the mass spectrometer.

The values of apparent concentration for the diverse additives were determined from the individual peak areas in the total ion chromatogram of each additive in relation to the area obtained for the internal standard, 8OCB. Absolute concentrations may be somewhat different since variations in response factors among the studied substances are expected. Anyway, the most relevant issue is the relative change of the different additives with degradation time, and that shall remain unaffected by considering or not the response factors.

The relative variation of some additives appearing in a small concentration has been evaluated under SIM mode from the analysis of the more representative m/z peak in the corresponding mass spectrum. This is the case of Tinuvin 770, which presents a rather prominent peak for m/z = 124, and also for Irganox 1076, which appears to coelute with the much more prominent signal of oxidized Irgafos 168 (see Figure 4). In this case, the selected m/z values were 515 and 530, which are distinctive of Irganox 1076 and not present in the mass spectra of oxidized Irgafos 168 (see Figure S4).

Identification of compounds was carried out, first, by matching their mass spectra vs NIST08 (US National Institute of Standards and Technology, Gaithersburg, MD) commercial library, with a probability above 90%. The identification was further ascertained by comparison with the corresponding pure compounds when these were available.

The studied compounds cannot always be found in the mass spectrometer software libraries (especially when the peaks correspond to degradation products identified from high-molecular-weight additives). In such cases, the assignment is made by comparing the expected fragmentation path from the most probable degradation products with that observed in the chromatogram.

In addition, the use of a linear retention index (LRI) turns out of practical importance. This approach is obtained from the elution times and is calculated taking into account the retention times of the unknown compound and those of the corresponding anterior and posterior eluting n-alkanes. The evaluation of the results of a hydrocarbon standard comprising between C12 and C49 has allowed establishing retention times from which it was possible to estimate the LRI for different compounds of interest found in the sample under analysis. These values, together with those of other many common additives and their degradation compounds, are collected in Figure S5 of the Supporting Information; also, their structures are given in Table S1.

The effect of photo-oxidation in the PP sample has been also studied by analyzing the evolution of carbonyl groups. For that, Fourier transform infrared spectra with attenuated total reflectance (FTIR–ATR) were recorded on a PerkinElmer Spectrum One spectrophotometer (PerkinElmer, Waltham, MA) with a resolution of 4 cm⁻¹.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03058.

Mass spectra and assignment of the degradation products of Irganox 1010 and Irganox 1330; whitening of the sample by the effect of photo-oxidation; mass spectra of oxidized Irgafos 168 and Irganox 1076; and values of the linear retention index for various additives and degradation products (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Ernesto Pérez — Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), 28006 Madrid, Spain; orcid.org/0000-0002-5144-9268; Phone: 34-912587577; Email: ernestop@ictp.csic.es

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