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Pyrolysis-Gas chromatography-Isotope Ratio Mass Spectrometry of polyethylene.

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Abstract

Polyethylene is probably the most used plastic material in daily life and its accurate analysis is of importance. In this communication the chemical structure of polyethylenes is studied in detail using conventional analytical pyrolysis (Py-GC/MS), bulk stable isotopic analysis (IRMS) and pyrolysis compound specific stable isotopic analysis (Py-CSIA) to measure stable isotope proportions ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and δD) of polyethylene pyrolysis compounds. Polyethylene pyrolysis yields triplet peaks of *n*-alkanes, α -alkenes and α,ω -alkanedienes. No differences were found for bulk $\delta^{13}\text{C}$ among different polyethylene types. However, conspicuous differences in δD were evident. It was possible to assign structure $\delta^{13}\text{C}$ and δD values to specific polyethylene pyrolysis products in the range 12-18 carbon chain length. Conspicuous differences were found for the pyrolysis products with unsaturated moieties showing significant higher δD values than saturated chains (alkanes) that were deuterium depleted. In addition, a full isotopic fingerprinting ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and δD) for a dye (*o*-chloroaniline) contained in a polyethylene is reported. To the best of our knowledge this is the first application Py-CSIA to the study of a synthetic polymer. This hyphenated analytical technique is a promising tool to study synthetic materials, providing not only a fingerprinting, but also allowing the traceability of the polymerization process and the origin of the materials.

Keywords

Plastics; Compound-specific isotope analysis; Hydrogen isotopes; Carbon isotopes; Nitrogen isotopes; Chloroaniline

1. Introduction

Polyethylenes, polyolefins or polyalkenes are a class of industrial polymers extensively used in the industry its internal structure depends on the arrangement of their ethylene monomers. In general, high density polyolefins (HDPE) are crystalline, whereas the low density polyolefins (LDPE) are amorphous. Polyethylene is highly versatile and probably the most used plastic material in daily life. The areas of applicability are still in continuous expansion to embrace a wide range of uses and therefore the analysis of polyethylene has been of importance since many decades.

The application of chromatographic techniques to the study of polymers is restricted due to their high molecular mass and low volatility. Analytical pyrolysis which combines GC/MS with pyrolysis has become an important tool for the characterization of polymers and polymer additives. Analytical pyrolysis is defined as the thermochemical decomposition of organic materials at elevated temperatures in the absence of oxygen [1]. The products of pyrolysis (pyrolysate) are amenable to chromatographic separation which, when combined with a mass spectrometry detector (Py-GC/MS), yields a valid fingerprint information about the molecular structure even of complex mixtures of natural and synthetic macromolecular substances [2], and is a proven useful technique for the analysis of synthetic polymers [3-6]. Pyrolytic techniques have well known additional advantages such are the requirement of small sample sizes and little to no sample preparation, being therefore convenient for inexpensive and relatively rapid analyses.

Pyrolysis-compound specific isotopic analysis (Py-CSIA), is a relatively novel technique in which the pyrolysate is directed, through a combustion (Py-GC-C-IRMS) or pyrolysis interface (Py-GC-TC), into an isotope ratio mass spectrometer (Py-GC-C/TC-IRMS) to measure stable isotope proportions i.e., $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and δD , $\delta^{18}\text{O}$ respectively of specific pyrolysis compounds. A schematic typical configuration of a generic Py-GC-C-IRMS device is described in [7].

It is accepted that the pyrolysis process does not produce appreciable fractionation of stable isotopes and therefore the pyrolysis products are considered to be isotopically representative of the starting material (Goñi and Eglinton, 1994; Corso and Brenna, 1997; Steinbeiss et al 2006) [8-10]. Therefore the above hyphenated analytical pyrolysis technique can provide valuable information on natural and synthetic materials, including not only their molecular fingerprinting, but also allowing the traceability of their formation processes and origin. In our case, we used the same chromatographic conditions in all the pyrolysis experiments (Py-

GC/MS and Py-CSIA). This matching permitted us to assign carbon, nitrogen and hydrogen isotopic values to specific peaks obtained by Py-GC-C/TC-IRMS analysis.

In this communication the chemical structure of low- and high-density polyethylenes is studied in detail by using conventional micro-furnace analytical pyrolysis, bulk stable isotopic analysis and pyrolysis compound specific stable isotopic analysis (Py-CSIA).

2. Experimental part

2.1. Materials

Three contrasting types of commercial manufactured polyethylene samples were analyzed: a high density polyethylene (HDPE) synthetic ice board used in skate rink, two low density polyethylenes (LDPE-a and LDPE-b) manufactured as bead toys and a very low density polyethylene (VLDPE) green color masterbatch.

2.2. Bulk C, H, N stable isotopic analysis (IRMS)

Bulk isotopic signature of light elements ($\delta^{13}\text{C}$, δD and $\delta^{15}\text{N}$) was analysed using a Flash 2000 HT (C, H, S) combustion (C) and (H, O) pyrolysis (TC) elemental micro-analyser coupled via a ConFlo IV interface unit to a continuous flow Delta V Advantage isotope ratio mass spectrometer (IRMS) (Thermo Scientific, Bremen, Germany) (C/TC-IRMS). Isotopic ratios are reported as parts per thousand (‰) deviations from appropriate standards recognized by the International Atomic Energy Agency (IAEA) [11]. The standard deviation of bulk $\delta^{13}\text{C}$ was typically less than $\pm 0.05\text{‰}$ and for bulk of δD less than $\pm 0.4\text{‰}$.

2.3. Conventional analytical pyrolysis (Py-GC/MS)

In order to obtain molecular information and unambiguously characterize the main pyrolysis products, a direct pyrolysis-gas chromatography–mass spectrometry (Py-GC/MS) was performed using a double-shot pyrolyzer (Frontier Laboratories, model 2020i) attached to a GC/MS system Agilent 6890N. Samples (0.5 mg) were placed in small crucible capsules and introduced into a preheated micro-furnace at (500 °C) for 1 min. The volatile pyrolysates were then directly injected into the GC/MS for analysis. The gas chromatograph was equipped with

a HP-5ms-UI, low polar-fused silica (5%-Phenyl-methylpolysiloxane) capillary column (Agilent J&W HP-5ms Ultra Inert, of 30 m × 250 μm × 0.25 μm film thickness (HP-5ms-UI). The oven temperature was held at 50 °C for 1 min and then increased to 100 °C at 30 °C min⁻¹, from 100 °C to 300 °C at 10 °C min⁻¹, and stabilized at 300 °C for 10 min. The carrier gas was helium at a controlled flow of 1 mL min⁻¹. The detector consisted of an Agilent 5973 mass selective detector, and mass spectra were acquired at 70 eV ionizing energy. Compound assignment was achieved by single-ion monitoring (SIM) for the major homologous series and by comparison with published data reported in the literature or stored in digital libraries (NIST and Wiley libraries).

2.4. Pyrolysis compound specific C, N and H isotopic analysis Py-CSIA

Direct pyrolysis compounds specific isotopic analysis (Py-CSIA) of light elements ($\delta^{13}\text{C}$ and δD) was carried out by coupling a double-shot pyrolyzer (Frontier Laboratories, model 3030D) attached to a GC/FID Trace GC Ultra system. At the end of the chromatographic column and to locate specific peaks within the chromatogram, the flux is divided and 10% diverted to a flame ionization detector (GC/FID) and 90% to a GC-Isolink System equipped with micro-furnaces for combustion set at 1000 °C (EA) and pyrolysis set at 1420 °C (TC) and coupled via a ConFlo IV universal interface unit to a continuous flow Delta V Advantage isotope ratio mass spectrometer (IRMS) (Thermo Scientific, Bremen, Germany) (Py-GC-(FID)-C\TC-IRMS).

Samples of 1–2 mg in weight were placed in small stainless steel crucible capsules and introduced into a preheated micro-furnace at (500 °C) for 1 min. The evolved gases were then directly injected into the GC/FID/IRMS system for analysis. The gas chromatograph was equipped with a low polar-polarity HP-5ms-UI -fused silica (5%-Phenyl-methylpolysiloxane) capillary column Agilent J&W HP-5ms Ultra Inert, of 30 m × 250 μm × 0.25 μm film thickness (Ref. HP-5ms-UI).. The oven temperature was held at 50 °C for 1 min and then increased to 100 °C at 30 °C min⁻¹, from 100 °C to 300 °C at 10 °C min⁻¹, and stabilized at 300 °C for 10 min using a heating rate of 20 °C min⁻¹. The carrier gas was helium at a controlled flow of 1 mL min⁻¹.

Isotopic ratios are reported as parts per thousand (‰) deviations from appropriate standards recognized by the IAEA [11]. The standard deviations of compound specific $\delta^{13}\text{C}$, δD and $\delta^{15}\text{N}$ was typically less than ± 0.1‰, ± 5‰ and ± 0.2‰ respectively.

Structural features of specific peaks were inferred by comparing and matching the mass spectra obtained by conventional Py-GC/MS with the Py-GC/FID and Py-GC/IRMS

chromatograms obtained using the same column type and identical chromatographic conditions.

3. Results and discussion

3.1. Polyethylene structure as seen by analytical pyrolysis (Py-GC/MS)

The thermal cracking caused by pyrolysis at 500 °C yielded typical products informing on the structure of the polyethylene. Figure 1 depicts the compounds released after pyrolysis from HDPE and VLDPE. Both pyrograms of polyethylene samples consisted of well-defined series of oligomers formed by hydrocarbon monomers with n -chain lengths in the range of 10 to 36 C atoms. A closer look revealed triplet peaks consisting of α,ω -dienes (terminally unsaturated dienes), α -alkenes and n -alkanes that eluted from the capillary column in this order. Under our experimental conditions the triplet peaks were clearly defined within the range C_{11} to C_{24} , not resolved in longer chain homologues due to co-elution. This pyrolysis pattern was similar for all samples which is in agreement with previous pyrolytic experiments findings [12, 13].

Pyrograms of the VLDPE revealed three peaks absent from the other polymers were detected at minutes 5.8 (A + B) and 9.0 (C), which were identified as *o*-chloroaniline, *o*-chloroacetanilide, and *o*-chlorophenyl isocyanate respectively, which were absent from the rest of samples (Fig. 1). These pyrolysis products arise most probably from the masterbatch's green dye. Also in the VLDPE a series of alkyl aldehydes were detected that were absent from the other plastics. It is remarkable to indicate the absence of plastizicers (dialkyl phthalates) in the pyrograms from all the plastics.

As shown in the example in Figure 2, the conventional mass pyrograms (Py-GC/MS) were later used a source of structural information to assign carbon, nitrogen and hydrogen isotopic values to specific peaks. This was done by matching the Py-GC/MS chromatogram with those of flame ionization (Py-GC/FID) and IRMS (Py-GC-C/TC-IRMS) analysis obtained using the same pyrolysis and chromatographic conditions in an instrument fitted with the same column type,.

3.2 Polyethylene bulk isotopic signature

The values obtained for $\delta^{13}C$ and δD in the each different polyethylene samples are shown in Figure 3. No significant differences were found for $\delta^{13}C$ among the different polyethylene

samples (HDPE= $-30.3 \pm 0.1\text{‰}$; VLDPE= $-30.1 \pm 0.4\text{‰}$; LDPE-a= $-30.4 \pm 0.6\text{‰}$; LDPE-b= $-29.6 \pm 0.1\text{‰}$) (Fig. 3A). However, conspicuous differences in δD (HDPE= $-102.4 \pm 0.6\text{‰}$; VLDPE= $-79.1 \pm 0.7\text{‰}$; LDPE-a= $-155.2 \pm 0.2\text{‰}$; LDPE-b= $-114.0 \pm 0.6\text{‰}$) were evident (Fig. 3B) with the VLDPE sample showing the lowest δD value and the low density polyethylene (LDPE-a) particularly deuterium depleted.

Despite the fact that a certain amount of N was present in the VLDPE, as seen by Py-GC/MS from the included dye, we were unable to record a consistent bulk $\delta^{15}\text{N}$ value for this sample probably due to a concentration of N below the detection limit.

3.3. Polyethylene C and N compound specific isotopic analysis (Py-GC-(FID)-C/TC-IRMS):

Compound specific values were obtained for the three main families of polyethylene pyrolysis products (α,ω -dienes, α -alkenes and *n*-alkanes). To the best of our knowledge and taken into consideration possible co-elutions, we confidently were able to assign structure $\delta^{13}\text{C}$ and δD values in the range of 12 to 18 carbon atoms. In general, the results showed a correspondence between the polyethylene bulk $\delta^{13}\text{C}$ values and those of individual alkyl molecules (Fig. 4). No significant differences were found between samples, but some dissimilarity was found among specific compounds within samples. For VLDPE and LDPE-b samples the carbon isotopic signature was similar in all pyrolysis compounds. The polyolefins from HDPE and LDPE-a showed differences mainly between double unsaturated subunits (dienes) and the other series (alkenes and alkanes) inside our working range but for homologues with 13 and 17 carbons.

The δD compound specific values (Fig. 5) practically mimic the bulk values. Nevertheless, remarkable differences were observed between the alkyl series (alkanedienes, alkenes and alkanes) within the different polyethylene samples. The unsaturated moieties (alkanedienes and alkenes) in VLDPE showed significant higher δD values than the saturated chains (alkanes) that were deuterium (^2H) depleted, in the order diene>alkene>alkane. The HDPE plastic presented a similar isotopic signature to that of VLDPE, however the mono-unsaturated chains were the heaviest (^2H enriched) in the order alkene>diene>alkane for HDPE. The δD isotopic data of the LDPE samples were similar to that of VLDPE with a higher proportion of light hydrogen (^1H) and δD values of unsaturated chains tending to converge with chain length.

Different types of polyolefins, like those indicated above, differs in the number of branches within its molecular semicrystalline structure and this difference is in turn responsible for the main properties of the plastic [14]. In this line the VLDPE sample is the less crystalline with the

highest number of branches and this implies the existence of more tertiary carbons in the structure with a higher reactivity than secondary carbons, and these even greater than the primary or terminal carbons [15] (Fig. 6).

The distribution of alkyl subunits obtained from pyrolysis is in agreement with the mechanism of thermal cracking as previously described [16, 17]. This is best explained by a free-radical mechanism where the predominant process appears to be the intramolecular transfer of radicals involving the H shift in the terminal free radical, producing internal free radicals which subsequently undergo a β -scission [14] (Fig. 7). In a first stage a breaking of the chains occurs, preferentially in the more reactive (weaker) tertiary carbon bond originating two radicals; one in a secondary carbon (7c) and the other one in a terminal carbon (7b). This scission is also probable in secondary carbons originating in this case two terminal radicals through a deprotonation reaction. In a second stage, the new terminal or primary carbon tends to attach to terminal alkyl radical ($\cdot\text{CH}_2\text{-CH}_3$) (Fig. 7d), which can be produced by the thermal cracking of alkylic homologues under pyrolytic conditions (7a*) and produces a saturated (alkyl) chain (7h). Simultaneously, in the new secondary carbon radical and in one of terminal carbons resulting from the scission in a secondary carbon, the bond between the α carbon and β carbon breaks leaving the α carbon with a free electron, which can be donated to the remaining carbon radical ($\text{C}\cdot$) to form a double bond, plus a free radical in β position (7f). The latter is prone to react with other radical saturating the rest of the structure (7e). If the produced alkene chain (7g) have another tertiary carbon the reaction could be repeated continuously to produce chains with two (dienes) or more unsaturations.

No large differences for the bulk $\delta^{13}\text{C}$ and compound specific signatures were found among different polyethylene types. All samples presented a similar compound specific carbon isotope close to that in the bulk ca. -30 ‰. This indicates that no C isotopic fractionation occur during the pyrolysis process and therefore the polyolefin isotopic differences probably reflect the isotopic signature of the original hydrocarbon stock used in casting the plastic.

On the other hand, polyolefin δD signature of specific compounds released after pyrolysis may be influenced by other factors apart from that of the original hydrocarbon stock and dependent, at certain extent, upon the polymerization process and conditions. Compound specific δD signatures in the alkyl series presented a different behavior depending on the polyethylene type. As seen in Fig.5, in all cases, the series of alkanes were ^2H depleted (light) as compared with the unsaturated series that were ^2H enriched (heavy). This can be explained as a fractionation effect during the production of unsaturated series, with the tertiary and the

deprotonated radical from a secondary scised carbon acting as ^2H concentrators during the polyethylene pyrolysis cracking. Taking into account the results obtained, we hypothesize that the terminal carbon radicals ($7a^*$) are depleted in deuterium, for this reason, the hydrogen isotopic signature in *n*-alkanes was lower than in unsaturated series (Fig. 7).

In the HDPE sample δD values for the alkene series was greater than that of the alkanediene series, being this different from other polyethylene samples analyzed where the diene chains were the heaviest. This effect may be a consequence of a higher structural crystallinity in HDPE, less packed and with a lower number of branches, and thereby the frequency of H transfers to form the unsaturated alkene is higher than for terminal unsaturated alkanediene.

In addition, we were able to obtain a full isotopic fingerprinting for *o*-chloroaniline ($\delta\text{D} = -79.7 \pm 2.7\text{‰}$, $\delta^{13}\text{C} = -27.1 \pm 0.6\text{‰}$ and $\delta^{15}\text{N} = 21.8 \pm 1.9\text{‰}$). This is the main pyrolysis product from the dye present in the green VLDPE masterbatch polyethylene and the sole N bearing structure in the polymer.

4. Conclusions

Different types of polyethylene produce similar typical pyrograms consisting of regular triplets of *n*-alkanes, α -alkenes and terminally unsaturated α,ω -alkanedienes. The polyethylene type dependent δD differences found for specific pyrolysis products with higher values in unsaturated moieties and deuterium depleted saturated chains may reflect structural aspects of the polyethylene depend upon the polymerization process and conditions.

Although this effect seems to be an isotopic fractionation during the production of *n*-alkanes with tertiary carbons acting as ^2H concentrators in the polyethylene pyrolysis cracking, this may also reflect relevant structural aspects of the plastic like crystallinity and molecular branching that is, in turn, dependent upon temperature and pressure during the polymerization process.

The Py-CSIA represents a promising technique with high potential for the study of polymers fingerprinting, origin, polymerization conditions and processes. Since the first adaptation of the Py-CSIA hyphenated technique for $\delta^{13}\text{C}$ by Goñi and Eglinton [8], and to the best of our knowledge this is the first report of Py-CSIA application to the simultaneous characterization of stable light elements C, N and H in a synthetic polymer.

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FIGURE CAPTIONS

Figure. 1. Example of polyethylene (VLDP and HDP) analytical pyrolysis (Py-GC/MS) showing the mass spectra of the pyrolysis products corresponding to the green dye in the masterbatch plastic.

Figure 2. Example of chromatogram correspondence for sample VLDPE. I) Py-GC/MS chromatogram (MS pyrogram); II) flame ionization (Py-GC/FID) (FID pyrogram); III) IRMS (Py-GC-C/TC-IRMS) ($\delta^{15}\text{N}$, $\delta^{13}\text{C}$ and δD) pyrograms. A+B indicates nitrogen pyrolysis compounds.

Figure 3. Polyethylene bulk isotopic signatures A) $\delta^{13}\text{C}$ value and B) δD value. Error bars indicate sample standard error (mean $\pm$ STD).

Figure 4: $\delta^{13}\text{C}$ compound specific values for the three main families of polyethylene pyrolysis products in the range C_{12} to C_{18} for the four studied samples. Error bars indicate sample standard error (mean $\pm$ STD).

Figure 5. δD compound specific values for the three main families of polyethylene pyrolysis products in the range C_{12} to C_{18} for the four studied samples. Error bars indicate sample standard error (mean $\pm$ STD).

Figure 6. Theoretical model for a low-density polyethylene. Blue balls are deuterions, white are hydrogens, dark gray are carbons and red indicate a tertiary carbon.

Figure 7. Theoretical model for the polyethylene thermal cracking and the formation of *n*-alkane, α -alkene and α , ω -alkanediene, by breaking the β carbon bonds. *) Polyolefin terminal chain part.

HIGHLIGHTS:

Polyethylene pyrograms consist of *n*-alkane, α -alkene and α,ω -alkanediene triplets

Saturated chains were found consistently deuterium depleted (low δD)

Fractionation occur during pyrolysis with tertiary carbons acting as 2H concentrators

This reflects structural aspects depend on polymerization process and conditions

First report of Py-CSIA application to the characterization of a synthetic polymer

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5