Journal of Chromatography A, 1388 (2015) 236–243

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Pyrolysis-gas chromatography–isotope ratio mass spectrometry of polyethylene☆

J.A. González-Pérez[a,*], N.T. Jiménez-Morillo[a], J.M. de la Rosa[a], G. Almendros[b], F.J. González-Vila[a]

[a] IRNAS-CSIC, Av. Reina Mercedes, 10, 41012 Seville, Spain
[b] MNCN-CSIC, c/Serrano 115-B, 28006 Madrid, Spain

ARTICLE INFO

Article history:
Received 17 December 2014
Received in revised form 13 February 2015
Accepted 13 February 2015
Available online 17 February 2015

Keywords:
Plastics
Compound-specific isotope analysis
Hydrogen isotopes
Carbon isotopes
Nitrogen isotopes
Chloroaniline

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 (δ^{13}C, δ^{15}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 δ^{13}C among different polyethylene types. However, conspicuous differences in δD were evident. It was possible to assign structure δ^{13}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 (δ^{13}C, δ^{15}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.

1. Introduction

Polyethylenes, polyolefins or polyalkenes are a class of industrial polymers extensively used in the industry and 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 as 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., δ^{13}C, δ^{15}N and δD, δ^{18}O, respectively, of specific pyrolysis compounds. A schematic typical configuration of a generic Py-GC-C–IRMS device is described in Ref. [7].

☆ Presented at the XIV Scientific Meeting of the Spanish Society of Chromatography and Related Techniques, 1–3 October 2014, Barcelona, Spain.

* Corresponding author. Tel.: +34 95 4624711; fax: +34 954624002.
E-mail address: jag@irnase.csic.es (J.A. González-Pérez).

http://dx.doi.org/10.1016/j.chroma.2015.02.039

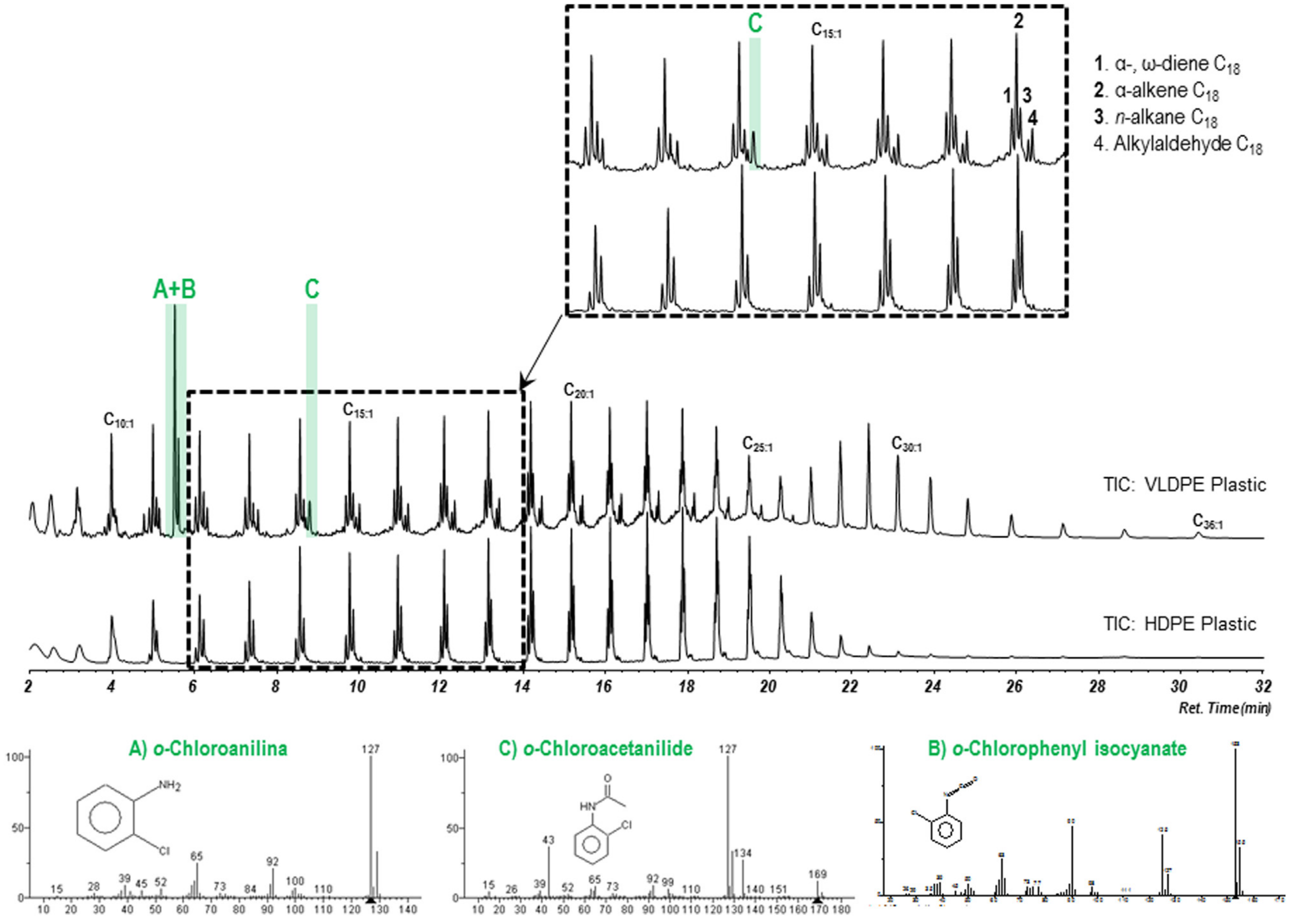

Fig. 1. Example of polyethylene (VLDP and HDP) analytical pyrolysis (Py-GC/MS) showing the mass spectra of the pyrolysis products corresponding to the green dye in the masterbatch plastic (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

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 [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 (δ^{13}C, δD and δ^{15}N) was analyzed using a Flash 2000 HT (C, H, S) combustion (C) and (H, O) pyrolysis (TC) elemental micro-analyzer 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 δ^{13}C was typically less than ±0.05‰ and for bulk of δD less than ±0.4‰.

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