

LINEAR LOW-DENSITY POLYETHYLENE COMPOSITION DETERMINATION WITH TGA-IST16-GC-MS COUPLING

Introduction

Polyethylenes constitute the most common industrial class of synthetic polymers with an annual global production of approximately 100 million tons.

Linear Low-Density Polyethylene (LLDPE) is produced by copolymerization of ethylene with an α -olefin which introduces short-chain branching (SCB) and thereby decreases the crystallinity of final polymer.

The most commonly used α -olefins for this purpose are 1-butene, 1-hexene and 1-octene which allow fine tuning of the crystallinity and thereby the properties of resulting polyolefin. The suitability for different applications can be achieved just by variation of the comonomer content thus it is of high interest to be able to measure the amount of these SCB.

Various analytical methods have been employed to determine the nature and degree of SCB.

The work described here, carried out jointly by SRA Instruments and the University of Lyon*, proposes a new coupling technique, which significantly increases the number of data points collected. It combines TGA, GC-MS and an innovative gas storage interface developed by SRA Instruments.

In order to identify the gaseous compounds emitted during thermal decomposition, TGA is generally associated to mass spectrometry and IR spectroscopy. However, for polymer with complex microstructures like LLDPE, IR and direct MS cannot unambiguously determine the nature of most components of gas mixtures. In these cases, coupling TGA with GC-MS offers promising advantages.

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TGA-IST16-GC-MS coupling technique

The on-line combination of GC-MS with TGA was applied to characterize gases released during the thermal degradation of the LLDPE samples.

Instrumentation :

- TGA : Mettler Toledo TGA/DSC 1, equipped with a DSC heat flow element for simultaneous detection of enthalpy variations
- IST16 : SRA Instruments gas storage interface, inserted between the TGA and the GC
- GC : Agilent Technologies 7890B GC
- MS : Agilent Technologies 5977C MSD



Fig. 1 – TGA-IST16-GC-MS coupling technique

Conduct of the experiments

Copolymers containing various proportions of 1-hexene and 1-octene were prepared using the zirconium catalyst $\text{rac-Et(Ind)}_2\text{ZrCl}_2$ activated with methylaluminoxane (MAO).

The average composition of the copolymers obtained was then elucidated using TREF, ^1H and ^{13}C -NMR spectroscopy.

Subsequently, the copolymers were further investigated by TGA-IST16-GC-MS.

Their characterization with this analytical system was compared to one of the polyethylenes prepared under similar conditions and used as reference.

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TGA-IST16-GC-MS experiments

1) *Thermogravimetric analysis (TGA)*

TGA was performed with a Mettler Toledo TGA/DSC 1, equipped with a DSC heat flow element for simultaneous detection of enthalpy variations. The temperature sensor of the equipment was calibrated using indium and zinc standards. All samples were accurately weighed (20 mg) into 150 μL aluminum oxide crucibles. The samples were heated from 40 to 600 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$ in dry nitrogen atmosphere at a flow rate of 30 mL min^{-1} .

2) *Storage interface (IST16)*

The composition of the gas mixture emitted during TGA experiment varies too quickly for a direct analysis by GC-MS instrument.

SRA Instruments developed a gas storage interface which allows to sequentially store in 16 loops, several fractions of the gaseous effluent from the TGA and to automatically inject these samples into GC-MS. The chromatographic separation time is then no longer a limitation for the detailed study of complex thermal analysis profiles.



Fig. 2 – IST16 Gas Storage Interface, SRA Instruments

The gases released during thermal decomposition were first collected in the IST16 device. A preheated transfer line between the TGA and IST16 storage device allowed the gases to enter one of the sixteen storage loops. These gases were stored until completion of the TGA run (Figure 3a). Afterwards, facilitated by the second transfer line connecting the IST16 with the GC, each fraction collected was injected into the chromatographic column for separation (Figure 3b).

Sixteen detailed gas chromatograms were acquired, and emitted compounds could be identified. All loops, valves and inert flow paths were installed in an isothermal oven and maintained at 250 $^{\circ}\text{C}$. The temperature of both transfer lines was set at 250 $^{\circ}\text{C}$. For all samples, the decomposition events took place between 400 and 540 $^{\circ}\text{C}$. The storage temperatures were therefore chosen accordingly, as listed in Table 1.

Table 1 – Corresponding storage temperatures and loop numbers

TGA: T [$^{\circ}\text{C}$]	–	400	420	430	440	450	460	470	480	490	500	510	520	530	540	–
IST16 loop ^{a)}	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16

The listed temperatures are the upper limits of the ranges.

^{a)} Loops 1 and 16 are used for blank samples before and after sample decomposition. No decomposition products were collected in these storage loops.

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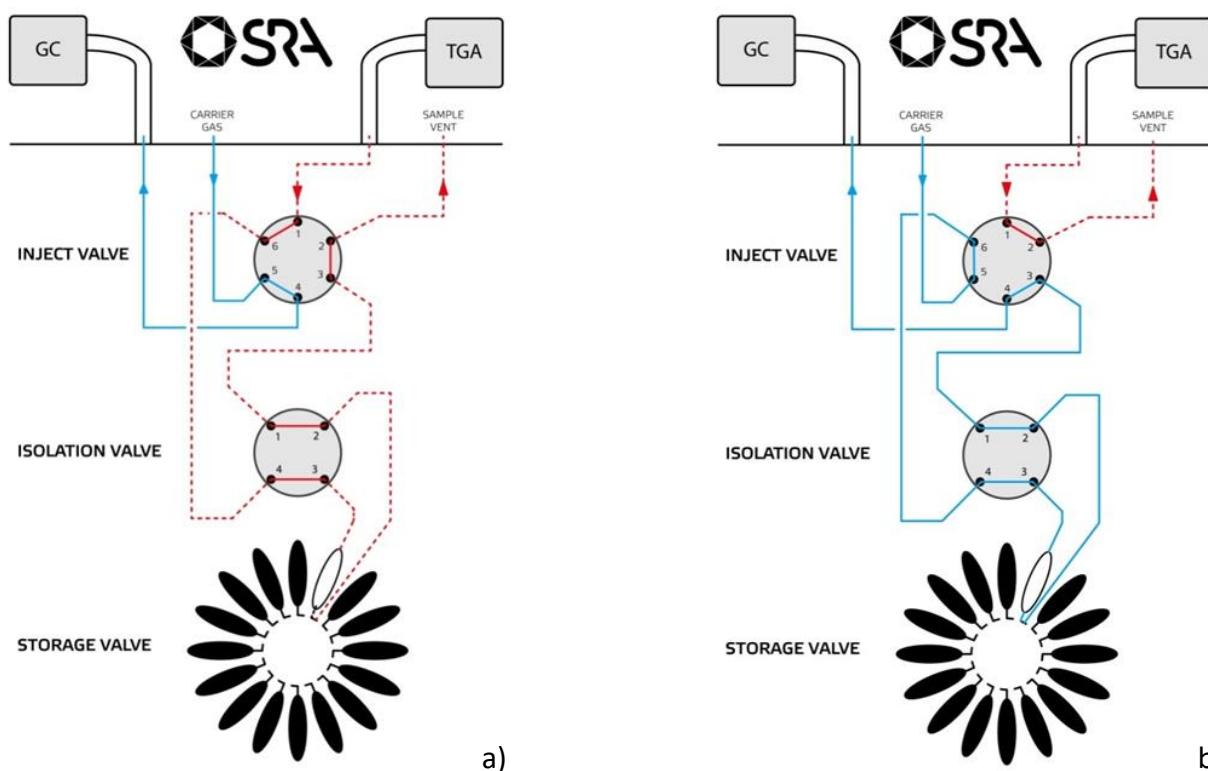


Fig. 3 – IST16 in storage mode a) and in injection mode b)

3) Gas chromatography – Mass spectrometry (GC-MS)

A 7890B GC instrument, equipped with a capillary column and a 5977C mass selective detector from Agilent Technologies were used.

Helium was selected as the GC carrier gas. The flow rate through the chromatographic column was set at 1 mL min^{-1} with a split ratio of 4:1. The column temperature was held initially at $40 \text{ }^\circ\text{C}$ for 10 min, increased up to $300 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$ and held at $300 \text{ }^\circ\text{C}$ for 24 min. The injector temperature was set to $280 \text{ }^\circ\text{C}$.

The mass spectrometer was operated in the conventional electron ionization mode at an electron multiplier voltage gain of 1 V/V, with a mass scan range from 5 to 500 amu at a scan rate of 5.6 sec^{-1} . The National Institute of Standards and Technology spectra library was used to identify the compounds.

Polymer characterization

The molar masses and the dispersity of polymers were determined by HT-SEC ; the TREF profiles confirmed that all copolymers are homogeneous in composition, as expected with a metallocene catalyst.

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Results and discussion

1) Thermal decomposition of the HDPE. This comonomer-free sample was used as a reference.

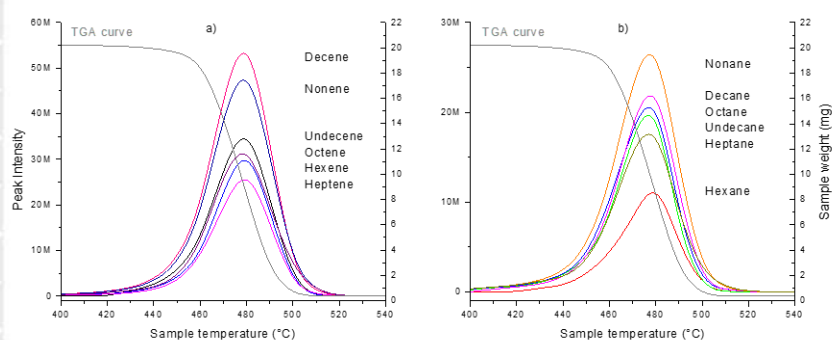


Fig. 4 – Emission profiles of a) alkenes and b) alkanes compounds from TGA analysis of sample 1 (HDPE).

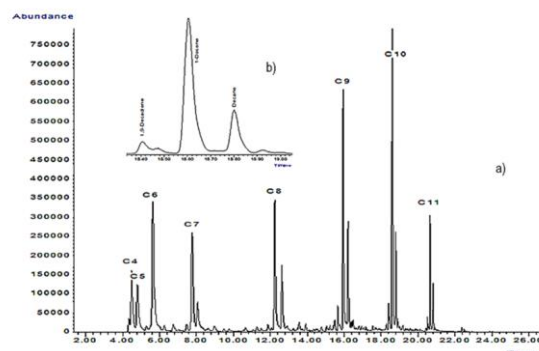


Fig. 5 – Mass spectrum (Total Ion Current) resulting from the thermal degradation of sample 1. a) total spectrum b) zoom on C10.

2) Thermal decomposition of Ethylene/Octene copolymers, under similar conditions.

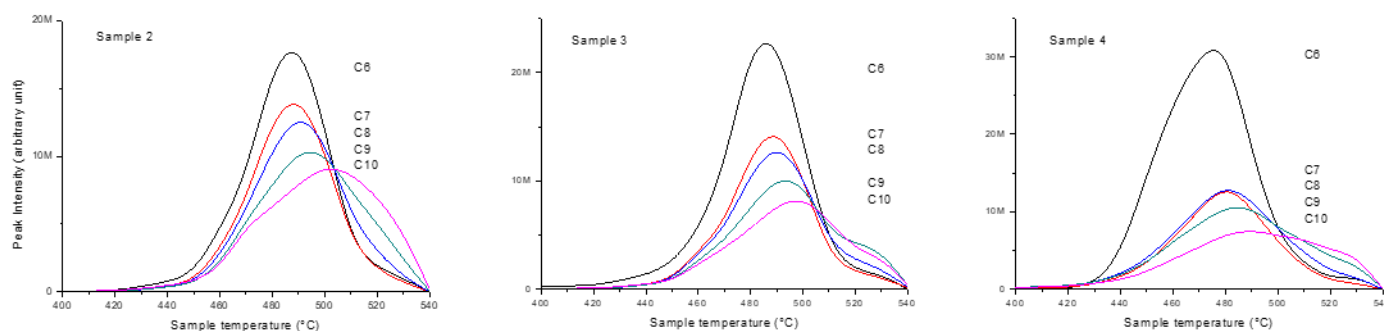


Fig. 6 – Emission profiles from the TGA analysis of ethylene/octene copolymers (sample 2, 3 and 4).

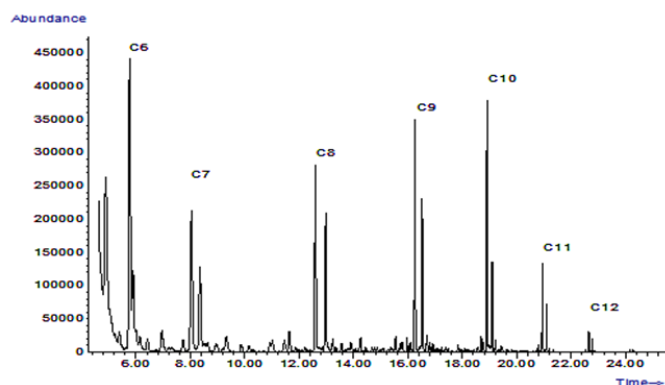


Fig. 7 – GC-MS result (extracted ion $m/z = 41$) for ethylene/octene copolymer, sample 3.

As in reference sample, the same distribution of three compounds (α , ω -diene, α -alkene, and n-alkane) was observed in Figure 7. In regard to LLDPE, new specific fragments predominate compared to the HDPE reference. The polymer chain breaks preferentially at the branches. Figure 6 clearly showed that C_6 compound (hexane and 1-hexene cumulated amounts), compared to other fragments, increase significantly as the octene content increases in the copolymer. It was therefore considered that the C_6 compounds are the main signature of ethylene/octene copolymers.

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3) Thermal decomposition of Ethylene/Hexene copolymers, under similar conditions.

When analyzing ethylene/hexene copolymers, a larger amount of C₄ compounds was identified in mass spectra as observed in Figure 8.

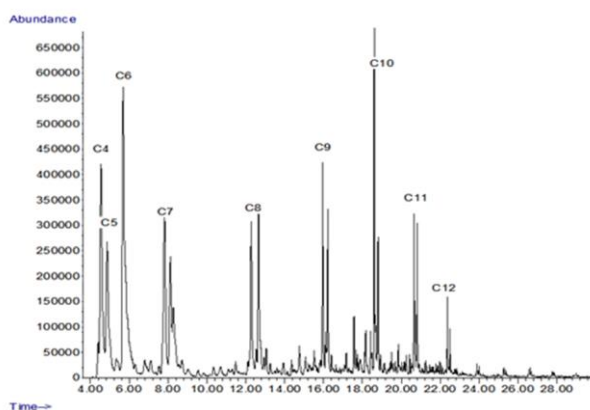


Fig. 8 – GC-MS result (extracted ion $m/z = 41$ or total ion current) for an ethylene/hexene copolymer, sample 8

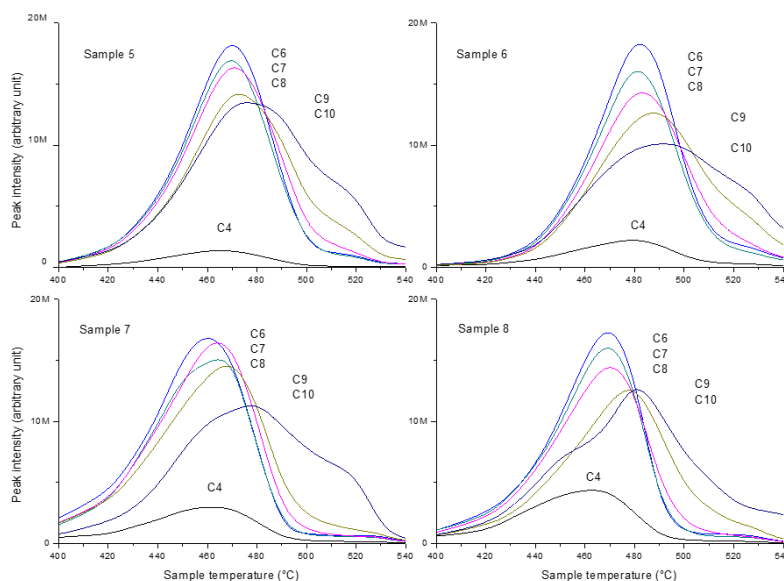


Fig. 9 – Emission profiles from the TGA analysis of ethylene/octene copolymers (sample 5-8).

Indeed, the thermal decomposition of ethylene/hexene copolymers leads to more butane and 1-butene signals in the corresponding spectra and C₄ content increases significantly as the hexene content increases in the copolymer (Figure 9). These C₄ fragments were the result of α -scissions on the butyl branch and were obtained in a similar way as C₆ fragments previously proposed for ethylene/octene copolymers.

Based on the strong correlation between the degradation products measured by TGA-IST16-GC-MS and the type of comonomer inserted into LLDPE, this method can provide very valuable information on the nature of branching. The sensitivity of this method is obviously high as low amount of comonomer, down to 0.5 mol% could be detected. Based on these results, the TGA-IST16-GC-MS system was calibrated and used in the following to efficiently quantify the amount of comonomer for unknown samples.

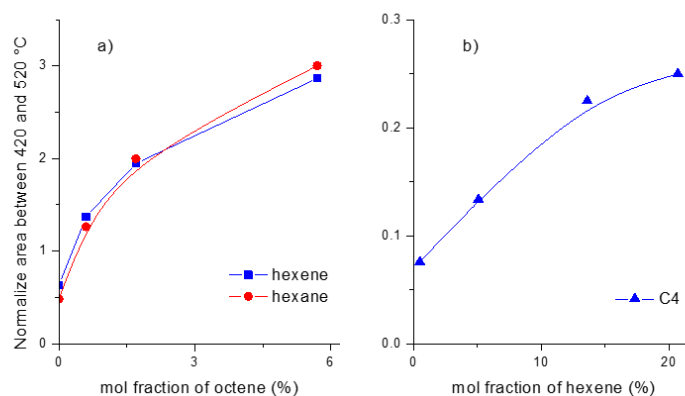


Fig. 10 – Calibration curve for
a) ethylene/octene copolymers obtained with samples 2 to 4
b) ethylene/hexene copolymers obtained with samples 5 to 8.

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The calibration curves show, that for low amounts of octene or hexene comonomers, the method is very sensitive because the slope of the curve is very high. This slope decreases and apparently ends up reaching a plateau beyond 20 mol% of hexene.

Conclusions

SRA Instruments developed an innovative gas storage interface (IST16), with a 16-loop fractions collector inserted between the TGA and the GC.

Thanks to this device, a TGA-IST16-GC-MS coupling system, working on an inert atmosphere, was used to provide further details on LLDPE composition.

Combining the versatility of thermal analysis and the accuracy and sensitivity of mass spectrometry, this original method allowed discriminating the comonomer type (hexene or octene) and content. Its main advantage is that various LLDPE decomposition products can be identified and quantified despite the very complex decomposition mechanism.

Moreover, it has the advantage of being quicker and more easily performed than traditional means of obtaining copolymer compositions such as nuclear magnetic resonance (NMR), or through separation techniques such as temperature rising elution fractionation (TREF).

TGA-IST16-GC-MS proved to be very useful for routine characterization of LLDPE and appears as a good substitute to NMR analysis that requires toxic solvent and long dissolution times.



Towards a potential application in the recycling field ?

The recycling process of plastic waste is of increasing economic and ecological importance. It is an objective that the recycling industry is trying to achieve. In order to identify different LLDPE to be recycled, the proposed approach can be effectively applied in a recycling process after specific separation step (flotation, magnetic, eddy currents...). LLDPE prepared by metallocene catalysis are of course simple samples with low chemical composition distribution and low molar mass dispersity. They have served as effective models for developing and validating the method. The study could be now generalized to more complex polyolefin like LLDPE resulting from heterogeneous catalysis or mixtures of different type of LLDPE as we can find during recycling process.

Acknowledgements

We thank Olivier Boyron, Dr Christophe Boisson and the "Chemistry and Processes of Polymerization" team of the CPE Lyon school C2P2 laboratory, for their work on the development of this new method.

For more information on the experiments carried out, here is the link of the publication :

<https://onlinelibrary.wiley.com/doi/pdf/10.1002/macp.201900162>