An Advanced Technique for Linear Low-Density Polyethylene Composition Determination: TGA–IST16–GC–MS Coupling

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Olivier Boyron*[2]; Tiffany Marre[1]; Alain Delauzun[1]; Ronan Cozic[1]; Christophe Boisson[2]

[1] *SRA Instruments, 210 rue des Sources 69280 Marcy l'Etoile, France*
[2] *Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Equipe LCPP, Bat 308F, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France; e-mail: olivier.boyron@univ-lyon1.fr*

Abstract

An innovative method based on thermogravimetric analysis combined with gas chromatography and mass spectrometry, TGA–IST16–GC–MS, was developed for measuring the comonomer type and the comonomer content in a series of linear low-density polyethylene (LLDPE). LLDPE such as copolymers of ethylene and octene or ethylene and hexene were synthetized using the $Et(Ind)_2ZrCl_2$ / MAO zirconium-metallocene catalyst. Their characterization with TGA-IST16-GC-MS system were compared to the one of polyethylene prepared under similar conditions and used as reference. TGA-IST16-GC-MS allowed discriminating the comonomer type (hexene or octene) and content.

Combining the versatility of thermal analysis and the accuracy and sensitivity of mass spectrometry, this original method proved to be very useful for routine characterization of LLDPE. It has the advantage of being quicker and more easily performed that traditional means of obtaining copolymer compositions such as nuclear magnetic resonance (NMR), or chromatographic methods such as TREF.

Keywords: polyethylene, linear low-density polyethylene, short-chain branching, thermogravimetric analysis, mass spectrometry

Introduction

Polyethylenes (PEs), which include low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE), constitute the most common industrial class of synthetic polymers with an annual global production of approximately 100 million tons[1, 2]. 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[3]. The most commonly used α-olefins for this purpose are 1-butene, 1-hexene and 1-octene[4, 5] 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. Therefore, it is of high interest to measure the amount of comonomer units (or SCB) incorporated into the PE chains.

Various analytical methods have been employed to determine the nature and degree of SCB. Spectroscopic methods like carbon-13 nuclear magnetic resonance ^{13}C-NMR[6-8] and infrared (IR) [9-12] have been widely developed to measure SCB. More recently liquid chromatography based on thermal fractionation has been developed by Wild, Monrabal, Soares, Cong and Macko through temperature rising elution fractionation (TREF)[13-15], crystallization analysis fractionation (CRYSTAF)[13, 15-18] and interactive liquid chromatography[19-23]. Thermal analysis with pyrolysis–GC[24-26] has been also employed to measure branching in PE.

This work proposes a new method based on thermogravimetric analysis (TGA). TGA is generally associated to mass spectrometry (MS) [27] and IR spectroscopy [28, 29] in order to identify the gaseous compounds emitted during thermal decomposition. 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. The emitted compounds are first separated by GC, then identified

and quantified by MS.

In this paper, an innovative coupling technic is introduced, which significantly increases the number of data points collected. It combines TGA, GC-MS and an innovative gas-storage interface (IST16) with a 16-loop fractions collector inserted between the TGA and the GC [30]. The analytical tool is called hereafter TGA-IST16-GC-MS and provides an efficient way to take advantage of the MS technique.

Copolymers containing various proportions of 1-hexene and 1-octene were prepared using the zirconium catalyst rac-Et(Ind)$_2$ZrCl$_2$ activated with methylaluminoxane (MAO) [31-33]. The average composition of the copolymers obtained was then elucidated using TREF, ^{1}H and ^{13}C-NMR spectroscopy. Subsequently, the copolymers were further investigated by TGA–IST16–GC–MS.

Experimental Part

Method of polymerization

Manipulation were performed in a dry-argon atmosphere, using Schlenk techniques. Metallocene complex rac-Et(Ind)$_2$ZrCl$_2$ and methylaluminoxane (MAO, 10 wt% in toluene) were purchased directly from Sigma-Aldrich. The comonomer, 1-hexene and 1-octene, were distilled over CaH$_2$. Toluene and n-heptane were dried over 3 Å molecular sieves.

Polymerizations were performed in a 500 mL glass reactor equipped with a blade stirrer and an external water jacket for temperature control as described in a previously article[34]. Polymerization was stopped by adding methanol and the mixture obtained was poured into methanol. The precipitated polymer was collected by filtration, washed with methanol, and dried under vacuum.

Characterization

High temperature size exclusion chromatography (HT-SEC)

HT-SEC analyses were performed using a Viscotek system, from Malvern Instruments SA, equipped with three columns (PLgel Olexis from Agilent Technologies, 300 mm × 7.5 mm, 13µm). 200 µL of a sample solution with a concentration of 5 mg mL^{-1} were injected and eluted in 1,2,4-trichlorobenzene at a flow rate of 1 mL min^{-1} at 150 °C. The mobile phase was stabilized with 2,6-di(tert-butyl)-4-methylphenol (200 mg L^{-1}) to avoid polymer degradation. Online detection was performed with a differential refractive-index detector and a dual light-scattering detector (LALS and RALS) for absolute molar mass determination. OmniSEC software version 5.2 was used for data acquisition and calculation.

NMR spectroscopy

The comonomer contents were determined by NMR spectroscopy using a Bruker Avance III 400 spectrometer operating at 400 MHz for ^{1}H-NMR and at 100.6 MHz for ^{13}C-NMR spectroscopy. ^{1}H-NMR and ^{13}C-NMR spectra were obtained at 90 °C with a 5 mm QNP probe and a 10 mm PA-SEX probe respectively. A 3:1 mixture of 1,2,4-trichlorobenzene and toluene-d_8 was used as the solvent. Chemical shifts were measured in ppm using the toluene signal (CHD$_2$ at 2.185 ppm) for ^{1}H-NMR spectroscopy and the polyethylene backbone signal (at 30.06 ppm) for ^{13}C-NMR spectroscopy.

^{1}H-NMR analyses were preferentially used to determine the α-olefin content in copolymers. The spectrum is composed of two main peaks: the signals of the CH$_2$ and CH protons of the polyethylene chain at 1.3 ppm and the signal of the methyl side groups at 0.9 ppm. Since high molar mass copolymers were prepared, the methyl chain ends were neglected.

However, at low comonomer contents (< 1 mol%, samples 2 and 5), the resolution obtained in the ^{1}H-NMR spectra was too low. In these cases, the ^{13}C-NMR spectra were used for the

determination of the α-olefin content as described in a previously article. [34]

Temperature rising elution fractionation (TREF)

TREF measurements were performed to measure the chemical composition distribution (CCD) of sample. They were carried out using a CRYSTAF-TREF 300 model manufactured by Polymer Char S.A. The fractionation in TREF is based on the progressive deposition of polymer with decreasing crystallinity on an inert support inside the column (150 mm × 9 mm). The polymer is thus segregated in layers with different chemical structures. Experimentally, 80 mg of sample were dissolved in 20 mL of 1,2,4-trichlorobenzene stabilized with 2,6-di(tert-butyl)-4-methylphenol at 150 °C. 0.5 mL of the sample solution was loaded into the column. The temperature was slowly decreased to 35 °C at a rate of 0.5 °C min^{-1} to allow the polymer to crystallize. A reverse cycle was performed to quantify these fractions by rinsing solvent through the column while gradually increasing the temperature at 1 °C min^{-1}. Eluted fractions corresponding to increasing crystallinity and decreasing comonomer content were thus obtained. The concentration of the polymer solution was monitored with an IR detector measuring the total CH absorption in the range from 2700 to 3000 cm^{-1}.

TGA–IST16–GC–MS experiments

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

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 °C to 600 °C at 10 °C min^{-1} in dry nitrogen atmosphere at a flow rate of 30 mL min^{-1}.

Storage interface (IST16)

The composition of the gas mixture emitted during TGA experiment varies too quickly for a direct analysis by GC–MS instrument. These 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 1a). Afterwards, facilitated by the second transfer line connecting the IST16 with the GC, each fraction collected were injected into the chromatographic column for separation (Figure 1b). Sixteen detailed gas chromatograms were acquired, and emitted compounds can be identified. All loops, valves and inert flow paths were installed in an isothermal oven and maintained at 250 °C. The temperature of both transfer lines was set at 250 °C. For all samples, the decomposition events took place between 400 °C and 540 °C. The storage temperatures were therefore chosen accordingly, as listed in Table 1.

Table 1. Corresponding storage temperatures and loop numbers.

TGA: T in °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.
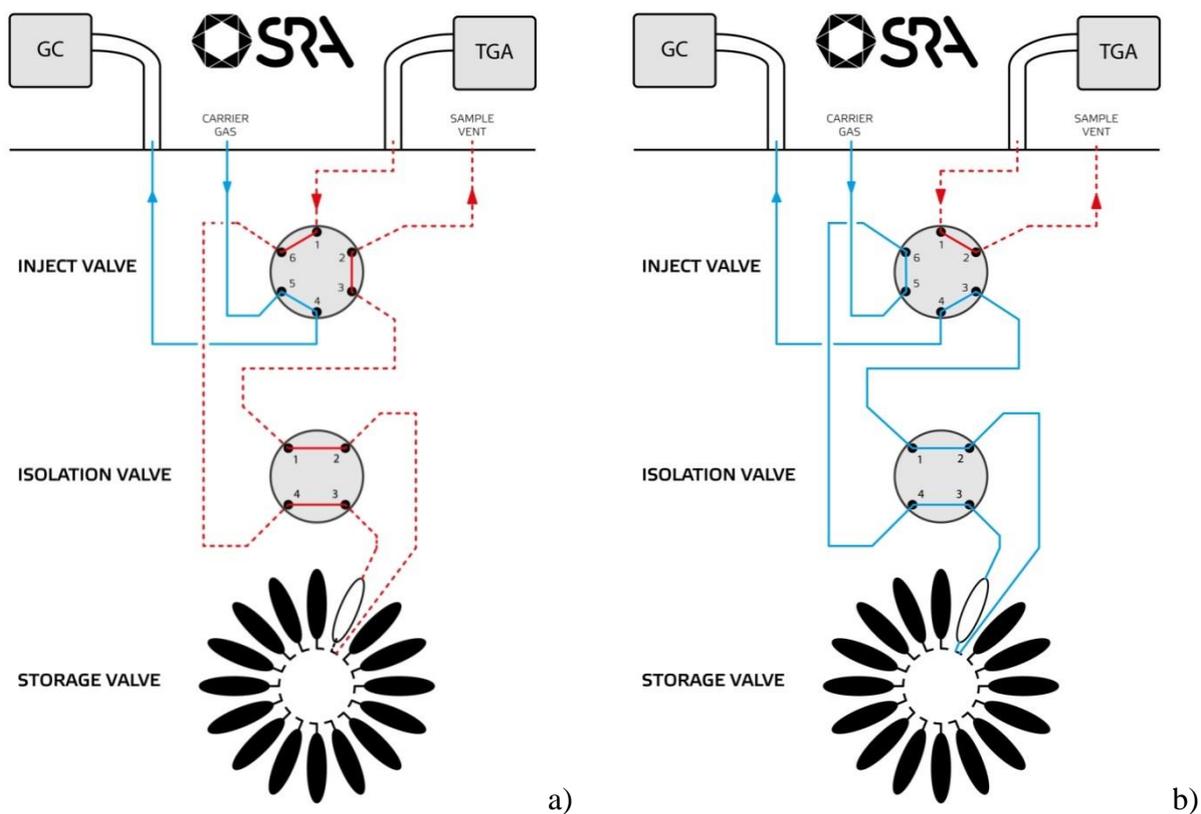
Figure 1. IST16 in storage mode a) and in injection mode b).

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 °C for 10 minutes, increased up to 300 °C at 10 °C min^{-1} and held at 300 °C for 24 minutes. The injector temperature was set to 280 °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.

Results and discussion

Copolymers of ethylene with 1-hexene or 1-octene (Table 2) were prepared using the zirconium-metallocene catalyst $Et(Ind)_2ZrCl_2$ / MAO. A homopolymer (HDPE - sample 1) was also synthesized and used as a reference. The comonomer distribution of the synthesized samples was measured by TREF and the comonomer content was determined by NMR spectroscopy. All samples were subsequently investigated by TGA–IST16–GC–MS coupling.

Polymer characterization

Table 2. Characterizations for the ethylene–α olefin copolymers.

sample	α-olefin	M_n $(Đ)$[a]	α-olefin content[b]	T_e[c]
		Kg mol^{-1}	mol%	°C
1	–	60.2 (2.9)	0	101.8
2	Octene	41.0 (2.6)	0.6	96.2
3	Octene	32.4 (1.8)	1.7	89.5
4	Octene	32.2 (1.8)	5.6	66.4
5	Hexene	24.4 (3.4)	0.5	97.7
6	Hexene	29.5 (1.8)	5.1	68.1
7	Hexene	26.4 (2.3)	13.6	*
8	Hexene	26.4 (2.3)	20.7	*

[a] Determined by HT-SEC with light scattering detector. $Đ$ = dispersity. [b] Determined by ^{1}H- or ^{13}C-NMR spectroscopy. [c] Elution temperature determined by TREF, * no peak observed in TREF experiment.

The molar masses and the dispersity of polymers were determined by HT-SEC (table 2). The copolymers exhibited a unimodal molar mass distribution. The TREF peak temperature of the samples gradually decreases as the comonomer content decreases, as observed in the previous works.[34, 35] Due to the high comonomer content in samples 7 and 8, the resulting copolymer

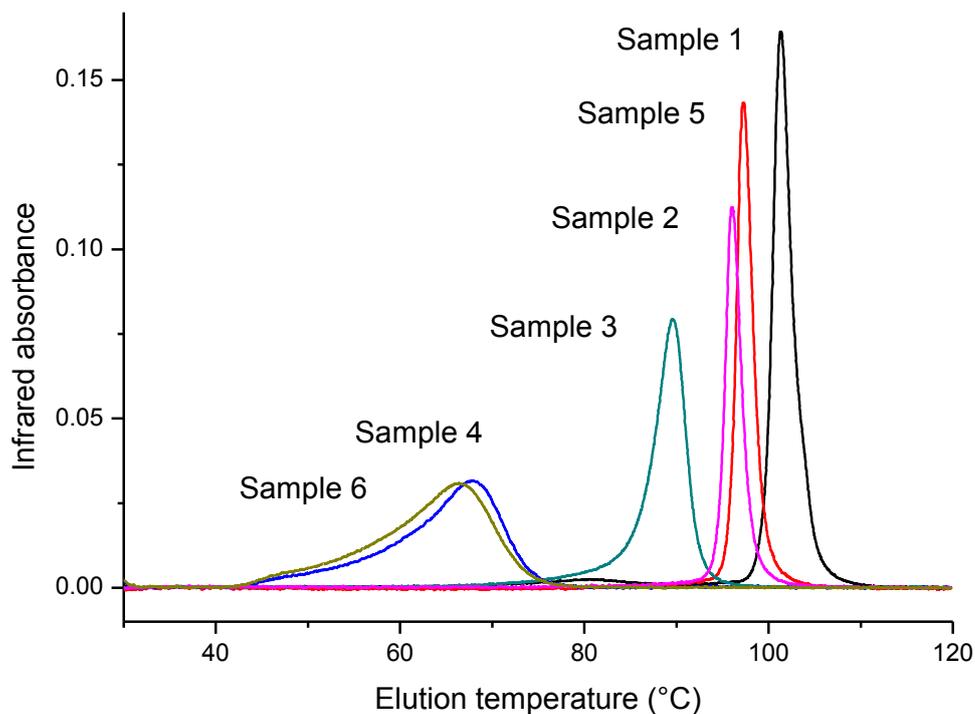are soluble at ambient temperature, and no peak was observed in TREF experiments.

Figure 2. TREF profile of poly(ethylene-co-octene) (samples 2-4) and poly(ethylene-co-hexene) (samples 5-8) copolymer with a crystallization rate of 0.5 °C min^{-1}

TREF profiles in Figure 2 show that the signals collected are rather narrow and confirm that all copolymers are homogeneous in composition as expected with a metallocene catalyst. Because of their uniform comonomer distribution the copolymers are further employed below as models for TGA-IST16-GC-MS measurements.

Thermal decomposition of the HDPE

The comonomer-free sample (sample 1), used as a reference, was analyzed first with the TGA-IST16-GC-MS setup. The TGA curve in Figure 4 shows that the thermal decomposition occurs

in a temperature range between 430 °C and 500 °C. Only one step of mass loss is observed in the thermogram of Figure 4.
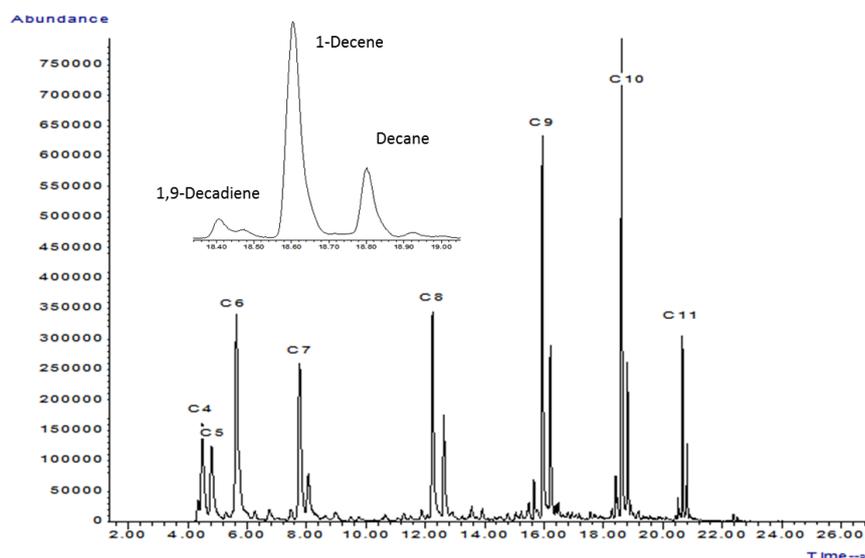

Figure 3. Mass spectrum (Total Ion Current) resulting from the thermal degradation of a HDPE polymer (sample 1). Each triplet consists of α, ω-diene, α-alkene and n-alkane at each carbon number. a) total spectrum b) zoom on C_{10}.

The mass spectrum of Figure 3 shows that HDPE typically cleaved in a specific manner and its thermal decomposition produced three types of aliphatic hydrocarbons: α, ω-diene, α-alkene, and *n*-alkane. Alkanes and alkenes were the main emitted products. The major compounds observed during the degradation contained 9 and 10 carbons.

The mechanism of thermal decomposition has been postulated in previous studies. [36-39] according to the authors, the thermal decomposition of PE is a radical chain reaction. It can be separated into 3 steps, comparable to the polymerization of vinyl compounds, with an initiation step, a depropagation step and a termination step.

The decomposition starts with a thermal homolytic chain scission at random locations in the chain backbone and leads to two radicals (Scheme 1a). Once radicals are made, the polymers go through a depropagation step with a hydrogen transfer reaction, which leads to the creation of an *n*-alkane fragment and a new radical (Scheme 1b). Radicals can decompose by β-scission

into α-alkene fragments (Scheme 1c). Finally, two radicals can react by coupling and disproportionation and lead to alkane and alkene fragments (Scheme 1d). This mechanism explains well the formation of n-alkane and α-alkene fragments that we observed during the thermal decomposition of sample 1.

Initiation

a)

Disproportionation

b)

c)

Termination

d)
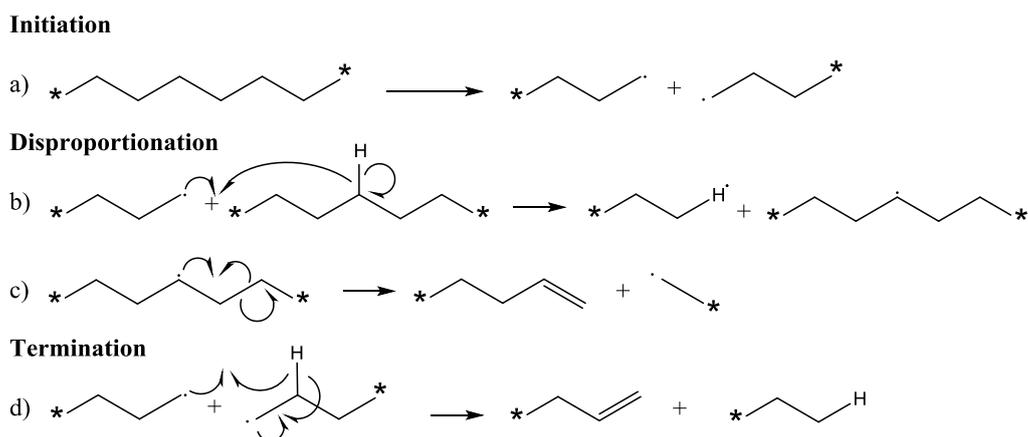
Scheme 1. HDPE decomposition into alkane and alkene a) thermal cleavage of HDPE into two radicals, b) intermolecular hydrogen transfer leading to an alkane fragment, c) β-scission of the radicals into α-alkene fragments d) radical disproportionation, in which 2 radicals form an alkane and an alkene fragment.
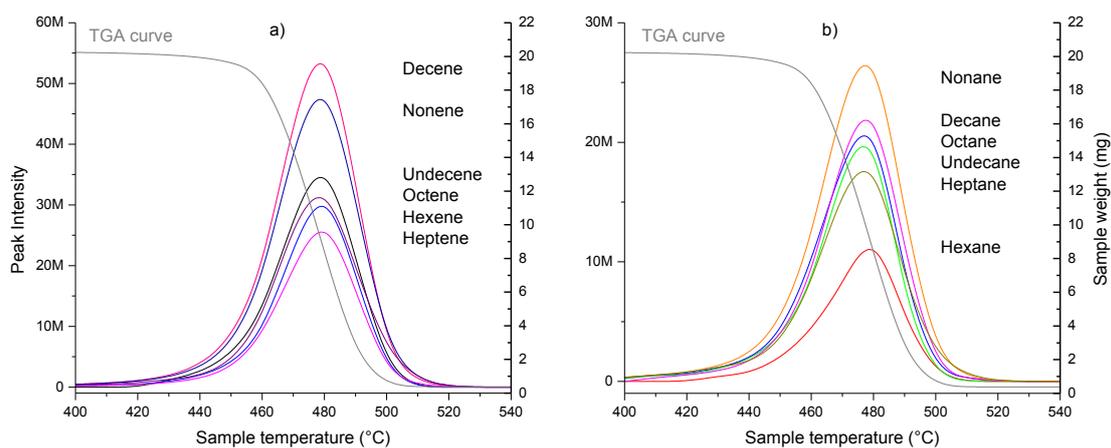

Figure 4. Emission profiles of a) alkenes and b) alkanes compounds from TGA analysis of sample 1 (HDPE). The left ordinate axis corresponds to the peak intensities in the gas chromatograms for each alkane and alkene component. The right ordinate axis refers to the TGA curve.

Figure 4 shows the amount of different main alkenes and alkanes observed corresponding to

different temperatures during TGA experiment. Each substance was identified by MS and its amount was calculated from the peak intensity in the gas chromatogram (Figure 3).

Minor amounts of cyclic compounds were also detected; in decreasing order, we found cyclopropane, cyclopentene, toluene, benzene, cyclohexene, cyclohexane and cyclopentane. For this work, we will focus on the major alkane and alkene degradation products from C4 to C11. Table 3 shows the retention time of the mean peaks observed in the mass spectrum and the name of the corresponding fragments.

Table 3. Alkenes and alkanes compounds and corresponding retention time.

Compound	1-Butene / butane	1-Pentene/pentane	1-Hexene	Hexane	1-Heptene	Heptane	1-Octene	Octane	1-Nonene	Nonane	1-Decene	Decane	1-Undecene	Undecane
RT (min)	4.6	5.1	5.8	5.9	8.0	8.3	12.6	12.9	16.2	16.5	18.6	18.8	20.6	20.8

Thermal decomposition of ethylene/octene copolymer

Degradation profiles were obtained for the ethylene/octene copolymers (samples 2, 3 and 4) under conditions similar to those used for the reference sample.
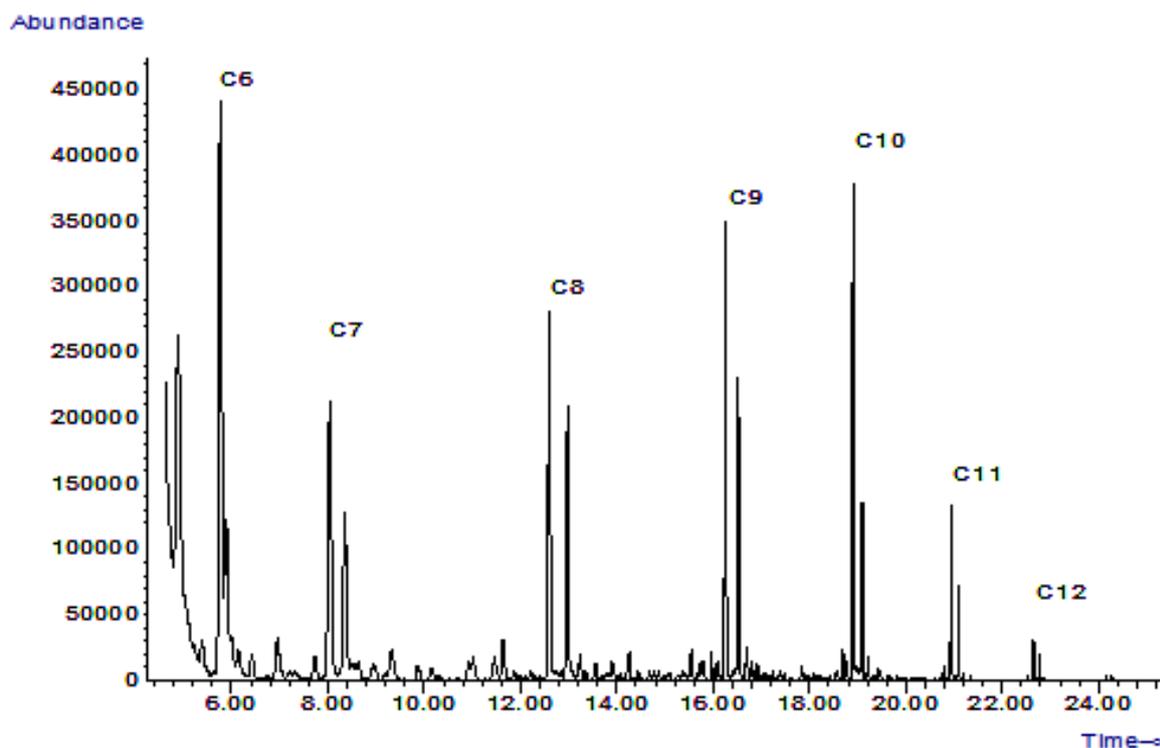
Figure 5. GC/MS result (extracted ion m/z = 41) for ethylene/octene copolymer, sample 3.

Similar to sample 1, the same distribution of three compounds (α, ω-diene, α-alkene, and *n*-alkane) were observed in Figure 5. In regard to LLDPE, new specific fragments predominate compared to the HDPE reference. The polymer chain breaks preferentially at the branches. This outcome relies on the branched structure of copolymers [40-42]. Ethylene/octene copolymers displays hexyl branches (C_6). As a result of the scission of these branches, the C_6 fragments increased significantly in the mass spectra. According to the mechanism proposed in Scheme 2, these fragments result from the α scissions on a tertiary carbon atom.
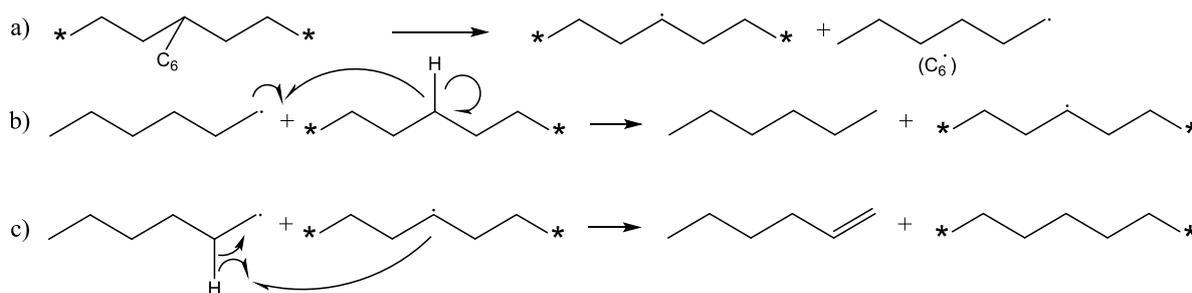
Scheme 2. Formation of hexane and hexene fragments for an ethylene/octene copolymer a) α scissions on a tertiary carbon atom, b) intermolecular hydrogen transfer leading to a hexane fragment, c) radical disproportionation, in which 2 radicals form an alkane and an hexene fragments.

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. We therefore considered that the C_6 compounds are the main signature of ethylene/octene copolymers.
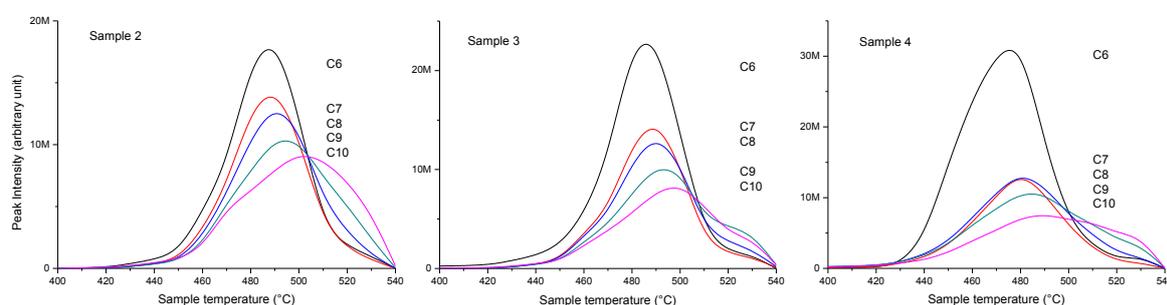

Figure 6. Emission profiles from the TGA analysis of ethylene/octene copolymers (sample 2, 3 and 4). The ordinate axis corresponds to the peak's intensities in the gas chromatograms for each component, alkane and alkene fragments were cumulated (C_6 = hexane and hexene fragments cumulated).

Thermal decomposition of ethylene/hexene copolymers

If C_6 fragments characterize ethylene/octene copolymers degradation, it would be expected that ethylene/hexene copolymers degradation would yield mainly to C_4 fragments.

When analyzing ethylene/hexene copolymers (samples 5 to 8), a larger amount of C_4 compounds was identified in mass spectra as observed in Figure 7.
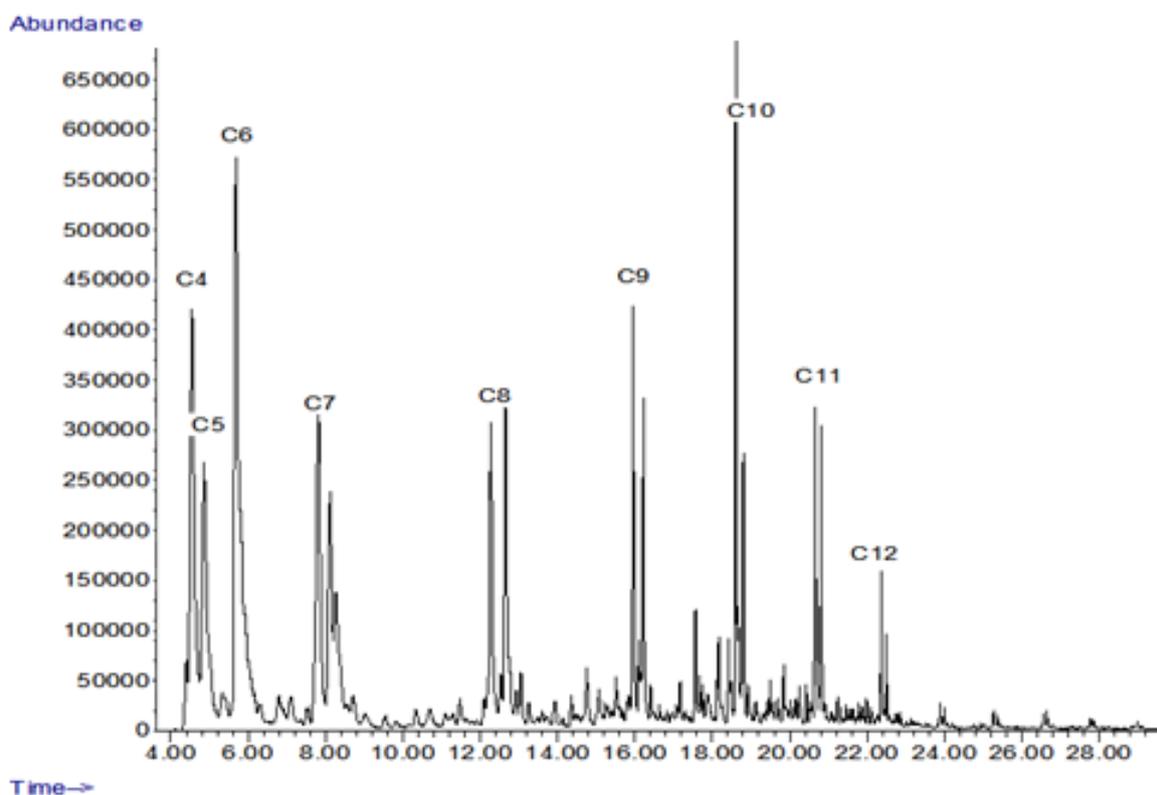
Figure 7. GC–MS result (extracted ion m/z = 41 or total ion current) for an ethylene/hexene copolymers, sample 8.

Indeed, the thermal decomposition of ethylene/hexene copolymers leads to more butane and 1-butene signals in the corresponding spectra and C_4 content increases significantly as the hexene content increases in the copolymer. This C_4 fragments were the result of α-scissions on the butyl branch and were obtained in a similar way as C_6 fragments previously proposed for ethylene/octene copolymers.
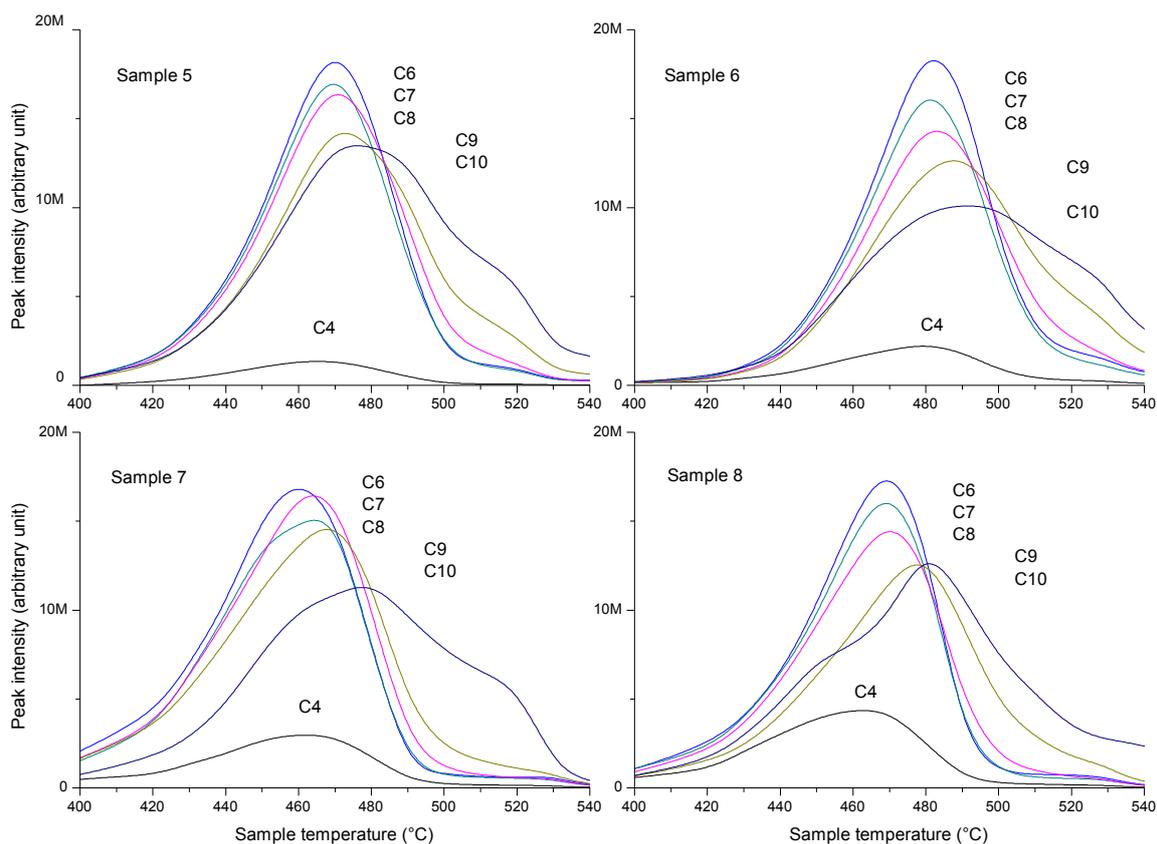
Figure 8. Emission profiles from the TGA analysis of ethylene/hexene copolymers (sample 5-8). The ordinate axis corresponds to the peak's intensities in the gas chromatograms for each component.

The scission mechanism proposed by Haney [36] supports the results observed with a main formation of C_4 compounds for ethylene/hexene copolymers and C_6 compounds 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, our TGA-IST16-GC-MS system was calibrated and use in the following to efficiently quantify the amount of comonomer for unknown samples.

Quantitative calibration

Since 1-hexene and hexane could be separated in the mass spectrum of ethylene/octene copolymer, two separate calibrations were performed, one from the hexane fragments and the other from 1-hexene fragments. Many parameters can affect the polymer degradation including the mass of samples, the contamination and the cleanliness of the system particularly of the transfer line. Thus, in order to normalize the peak intensities of hexane and 1-hexene, we used the peak of decane and 1-decene as internal standards, respectively. This assumes that decane and 1-decene were produced by the polymer backbone degradation independently of the comonomer content. Then, the area ratios obtained were plotted as a function of the comonomer content previously determined by NMR (Table 2) to construct the calibration curves.

For ethylene/octene copolymers (samples 2-4), two curves were created. In Figure 9a), the curve based on alkane detection displays $\sum_{420°C}^{540°C} \frac{\text{area of hexane peak}}{\text{area of decane peak}}$ and the curve based on alkene detection displays $\sum_{420°C}^{540°C} \frac{\text{area of hexene peak}}{\text{area of decene peak}}$ versus the mole fraction of octene inserted in the copolymer and measured by NMR. Sample 1 was used as a reference and provided the background signal value of hexane and 1-hexene fragments for an unbranched polymer.

For ethylene–hexene copolymers (samples 5-8), only one curve was created because the butane and the 1-butene fragments were not resolved by GC-MS. The curve in Figure 9b) shows $\sum_{420°C}^{540°C} \frac{\text{area of C4 peak}}{\text{area of C10 peak}}$ versus the mole fraction of hexene inserted in the copolymer and measured by NMR. Sample 1, which had no branching, was again used as a reference.
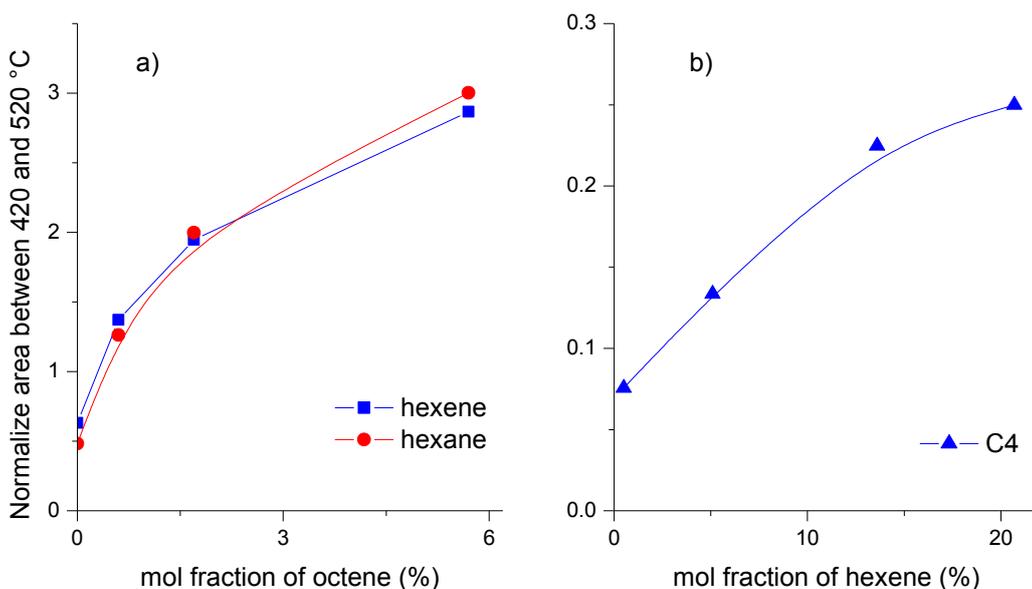
Figure 9. Calibration curve for a) ethylene/octene copolymers obtained with samples 2 to 4 b) ethylene/hexene copolymers obtained with samples 5 to 8. Hexene and hexane fragments measured during the degradation of ethylene/octene copolymers between 420°C and 540°C. C_4 fragments measured during degradation of ethylene/hexene copolymer between 420°C and 540°C.

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

The present paper describes a novel approach based on thermal degradation for the assessment of degree of SCB in LLDPE samples. This method was applied for two class of prepared homemade LLDPE. Ethylene/hexene and ethylene/octene copolymers were synthesized with a metallocene complex catalyst and characterized by HT-SEC and TREF to assess their homogeneity. SCB or comonomer content were measured by NMR. The TGA–IST16–GC–MS coupling system, working on an inert atmosphere, was used to provide further details on LLDPE composition. Its main advantage is that various LLDPE decomposition products can be

identified and quantified despite the very complex decomposition mechanism.

As previously described, alkane, alkene and diene fragments were observed from LLDPE degradation. In addition, we also observed aromatic compounds like benzene, toluene and cyclopentene.

This novel approach allows determining the nature of SCB in copolymers. We demonstrated that during the degradation of LLDPE, a major detection of C_4 fragments or C_6 fragments was respectively signature of ethylene/hexene or ethylene/octene copolymers. With the help of a calibration created during this work, co-monomer content could be determined. This method appears as a good substitute to NMR analysis that requires toxic solvent and long dissolution times.

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Table of content

An innovative technique TGA-IST16-GC-MS, thermogravimetric analysis combined with gas chromatography and mass spectrometry, was used to characterize LLDPE. The IST16 interface collects the gases produced during the degradation of the copolymer before GC-MS analysis. A specific signature of the comonomer present in LLDPE is identified and used for quantitative analysis of comonomer content.