# TGA/IST16/GC-MS COUPLING

## FOR STUDY OF α-OLEFIN CONTENT IN POLYETHYLENE

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## INTRODUCTION

Polyethylenes (LDPE, LLDPE, HDPE) are the most widely made synthetic polymers in volume with a production of around 75 MT a year. Their physical properties depend tremendously on their structure, so it is important to have rapid method to characterize chain composition. The average composition of the copolymers was measured using 1H, 13C NMR and TREF. Copolymer composition was then investigated by coupling of the TGA with the GC-MS technique to get rapid information about their structure.

An innovative TGA/IST16/GC/MS coupling is presented that significantly increase the number of data collected and thus provides an efficient way to take advantage of the GC/MS technique. The configuration uses a fractions collector inserted between the TGA and the GC. With materials such as LLDPE, the majority of the gaseous components leaving a TGA cannot be identified precisely with MS or IR. In this case, coupling of the TGA with the GC-MS technique offers interesting advantages. The emitted compounds are first separated by gas chromatography (GC) then identified and quantified by MS.

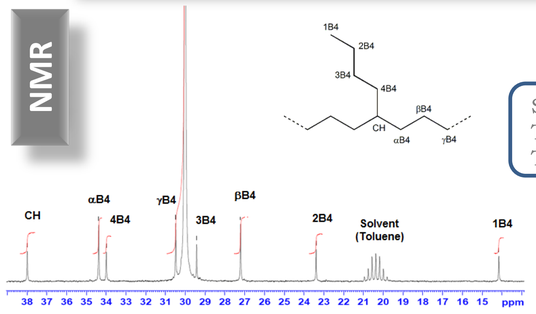
## POLYMERIZATION CONDITIONS OF STANDARDS

| α-olefin | 1-hexene | 1-octene | Norbornene |
|---|---|---|---|
| Solvent | Heptane | Heptane | Heptane |
| Catalytic system | $Et(Ind)_2ZrCl_2$ + MAO (Al/Zr = 2000) P = 4 bars T = 80°C | $Et(Ind)_2ZrCl_2$ + MAO (Al/Zr = 2000) P = 4 bars T = 80°C | $Et(Ind)_2ZrCl_2$ + MAO (Al/Zr = 1000) P = 3 bars T = 70°C |

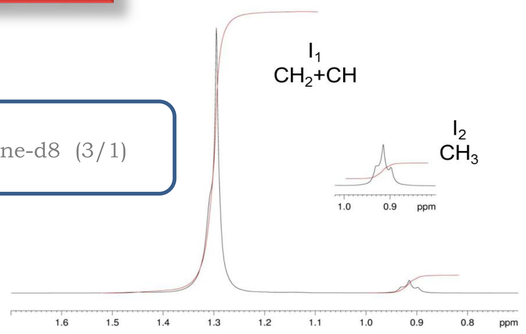
All polymerization experiments were performed in a 0.5 L glass reactor equipped with an injection chamber for the precatalyst [1].

## QUANTIFICATION OF COMONOMER CONTENT

### NMR




Solvent:
TCB/toluene-d8 (3/1)
T = 100°C



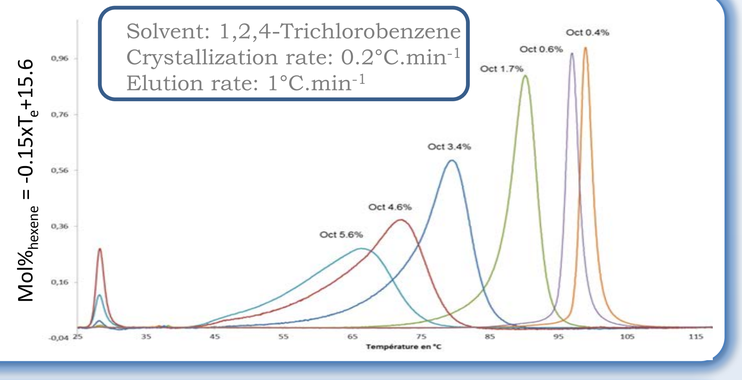

**Mol% of comonomer <1%**
Low resolution of $^1H$ NMR spectra: quantification by $^{13}C$ NMR

**Mol% between 1 and 4 %**
$^1H$ or $^{13}C$ (similar results)

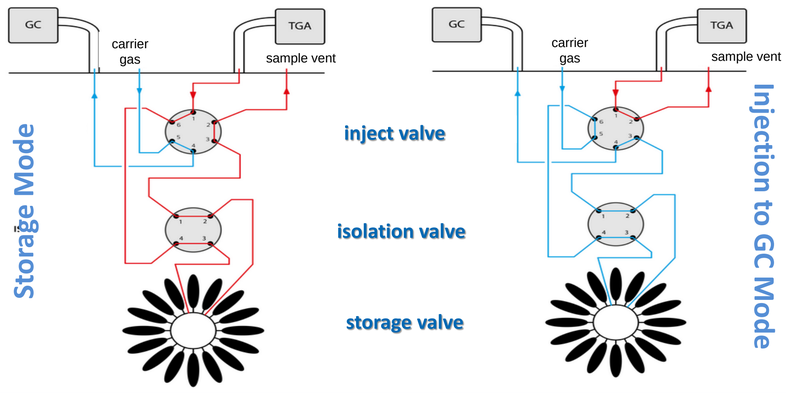
**Mol% of comonomer >4%**
Quantification by $^1H$ NMR

### TREF

Solvent: 1,2,4-Trichlorobenzene
Crystallization rate: 0.2°C.min$^{-1}$
Elution rate: 1°C.min$^{-1}$




## INSTRUMENTATION IST16


- Number of loop: 16 in Sulfinert™ stainless steel [2]
- Loop volume: 250µL in standard, customized volume on demand
- 2 heated zones
- Heated transfer lines: low internal diameter x 1.15 meter in Sulfinert™ stainless steel
- Valve box temperature: 250°C as standard working temperature (300°C can be reached for some special applications)

## THERMAL DECOMPOSITION OF DIFFERENT LLDPE

### Alkenes Profile for homo PE

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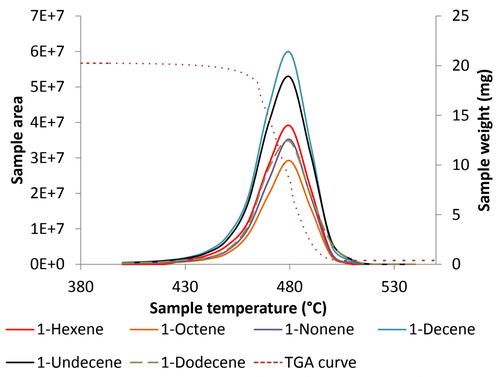
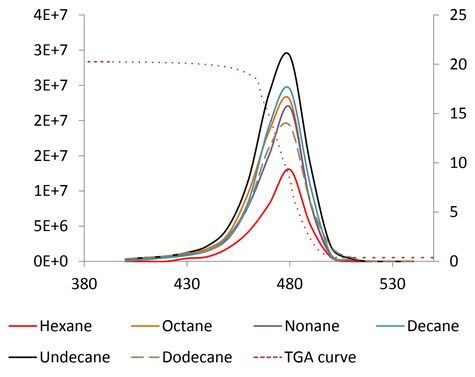
Gas : Nitrogen (30 mL/min.) - Analysis rate: 40 to 600 °C at 10°C.min$^{-1}$

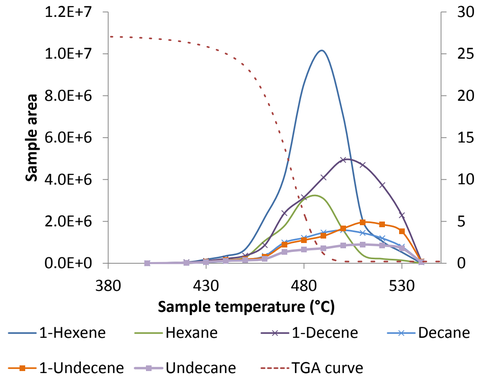


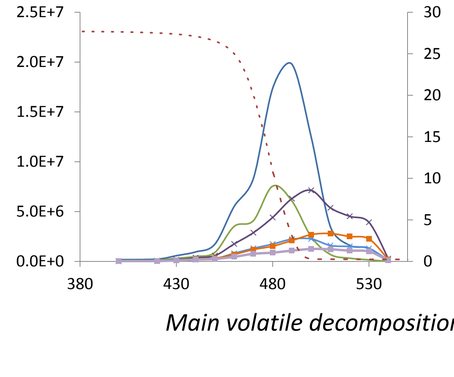



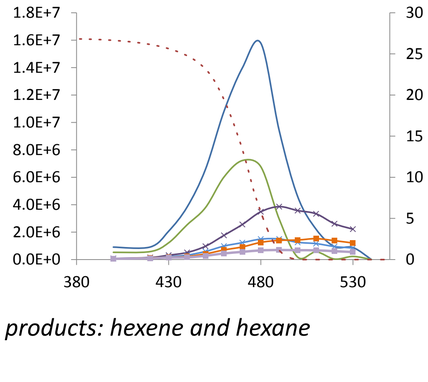

*Decene/decane and undecene/undecane are the main volatile decomposition products*

### P(E/Octene) 0.4 mol% 1.7 mol% 5.7 mol%

Gas : Nitrogen (30 mL/min.) - Analysis rate: 40 to 600 °C at 10°C.min$^{-1}$



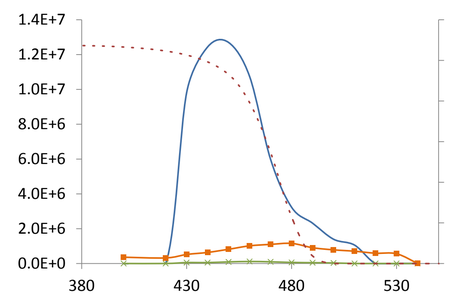


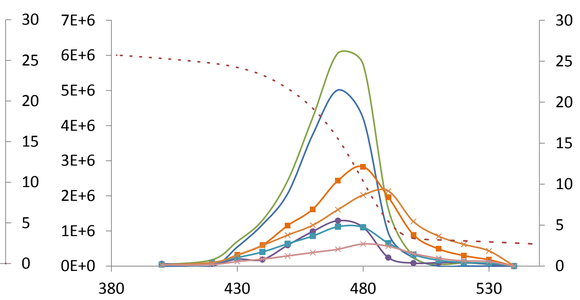
*Main volatile decomposition products: hexene and hexane*

### P(E/Hexene)

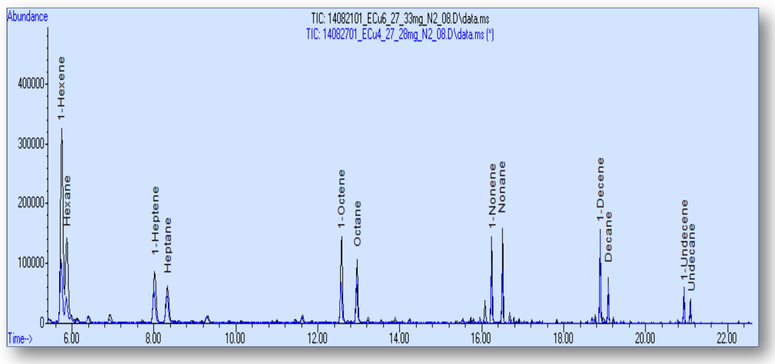
### P(E/Norbornene)

Gas: Helium (30 mL/min.) - Analysis rate: 40 to 600 °C at 10°C.min$^{-1}$



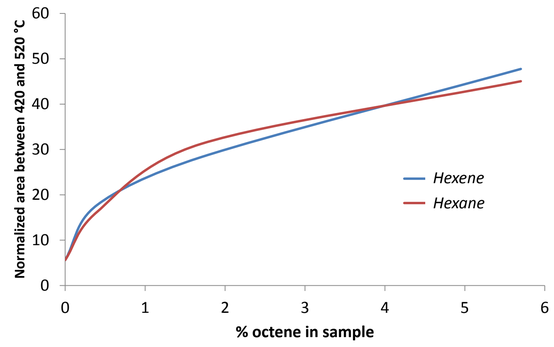




### TIC for P(E/Octene) 0.4mol% and 5.7 mol% (Loop n°8)




*Hexane and hexene signals increase with the quantity of octene in the sample*

### Calibration Curves of P(E/Octene)




*Normalized curves with $C_{10}$ peak area for hexane and hexene*

## CONCLUSION

The innovative TGA/IST16/GC/MS coupling is a powerful and versatile tool for interpretation of LLDPE structure.
For an **homopolymer** the main volatil decomposition products are **decane/decene** and **undecane/undecene**.
For an **ethylene/hexene** copolymer the main decomposition products are **butane and butene**.
For an **ethylene/octene** copolymer the main decomposition products are **hexane and hexene**.
TGA/IST16/GC/MS coupling is shown to be a viable technique to obtain qualitative and quantitative information on α-olefin content in LLDPE. The quantity of the degradation product is directly proportional to the inserted co-monomer content.

## REFERENCES

[1] E Cossoul, L Baverel, E Martigny, T Macko, C Boisson, O Boyron , Macromolecular Symposia, 330,42-52 (2013)
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