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DE LA RECHERCHE À L'INDUSTRIE



A comparison of ASAP and DART ionizations for the analysis of polyurethanes and their additives

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SMAP 2015 – AJACCIO- FRANCE

Polyurethane (PU)

- Among the most used copolymers
- One of the most versatile material
- Applications



Flexible foam
in upholstered furniture



Coatings, Adhesives, Sealants



Rigid foam
in construction insulation or automobile

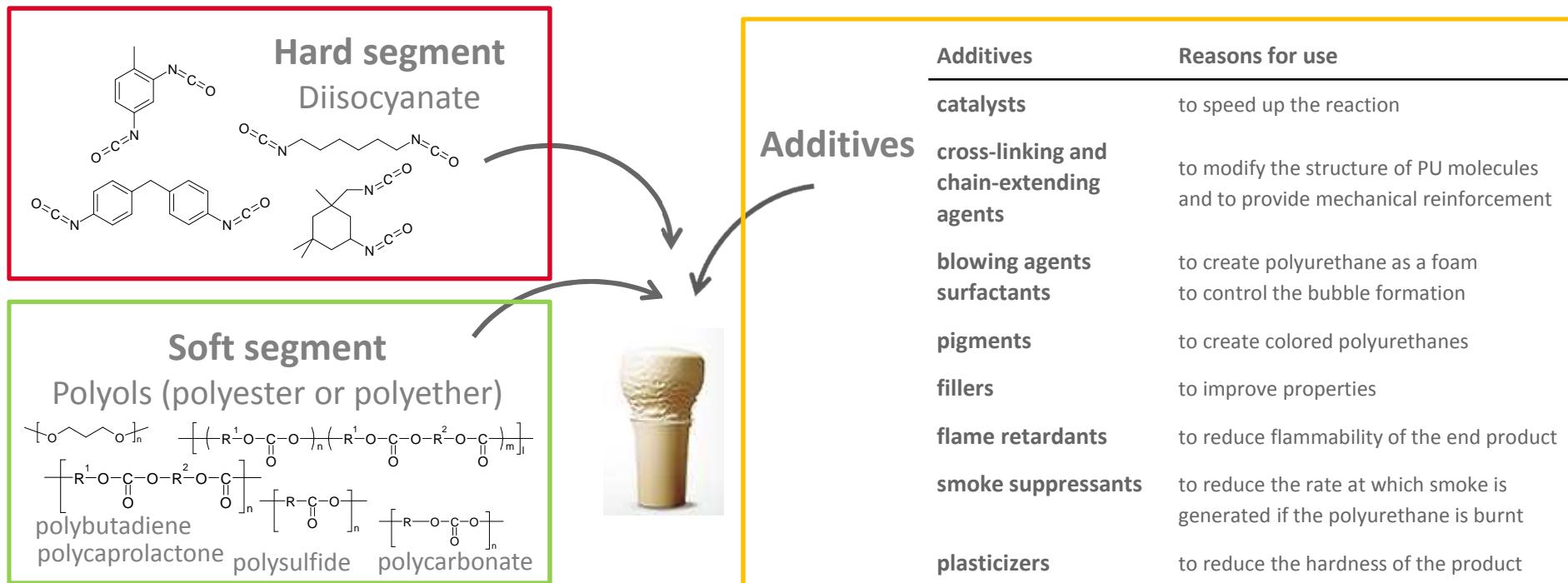


Thermoplastic polyurethane
in medical devices and footwear

- According to their chemical composition => different properties -> applications

Polyurethane synthesis

- Polyaddition of a diisocyanate to a polyol in the presence of additives

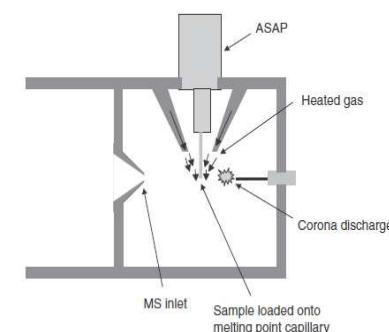
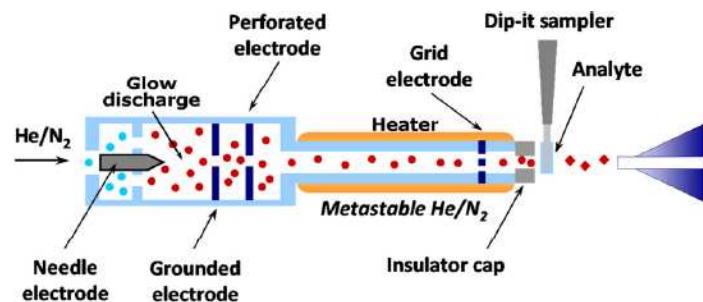


- Complex composition and different structures
 - Copolymer → difficult to characterize directly by MS without sample treatment:
 - preliminary dissociation of each segment from the copolymer (e.g. pyrolysis or chemical dissociation)
 - Py-GC/MS and/or MALDI/MS
- ⇒ Aim: direct analysis of PU by mass spectrometry

AMBIENT MASS SPECTROMETRY

THERMAL - PLASMA SOURCES

	DART (Direct Analysis in Real Time)	ASAP (Atmospheric Solid Analysis Probe)
Samples	liquid or solid samples	
	Use of pure sample	
	Direct analysis of the sample	Sample deposited onto glass tube
Analyzed compounds	Non polar to polar Volatile or semi-volatiles	
Sample desorption	Desorption using a hot metastable He/N ₂ flux	Desorption of solid in hot gas stream (N ₂)
Ionization	Ionization by excited He atoms produced from a corona discharge	Ionization from plasma generated by a corona discharge
Produced ions	Positive mode: M ⁺ , [M+H] ⁺ , [M+O+H] ⁺ , [M+NH ₄] ⁺ Negative mode: M ⁻ , [M-H] ⁻ , [M-H+O ₂] ⁻ , [M+O ₂] ⁻ , [M+OH] ⁻	Positive mode : M ⁺ , [M+H] ⁺ Negative mode: [M-H] ⁻



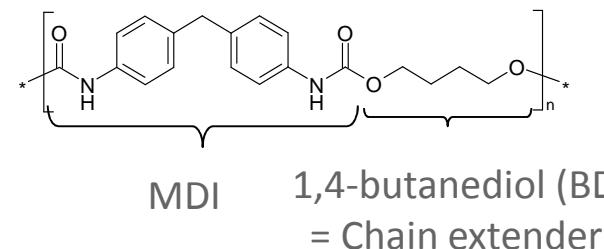
Industrial samples

wind-sock used for
laboratories air extraction

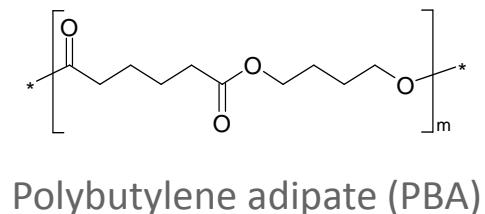
**Polyester
PU**



Hard Segment



Soft Segment

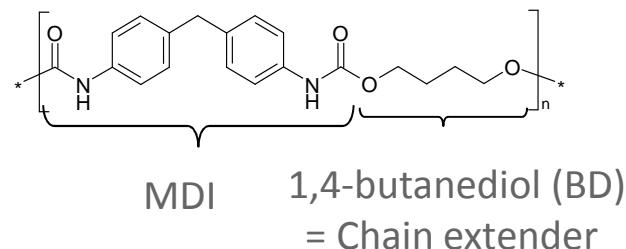


Electric cable sheath

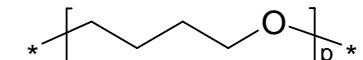
**Polyether
PU**



Hard Segment



Soft Segment

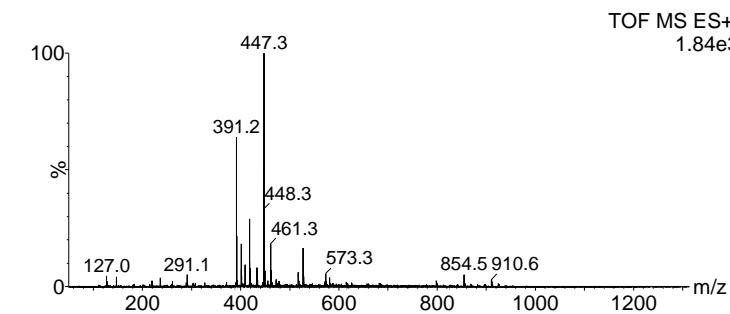
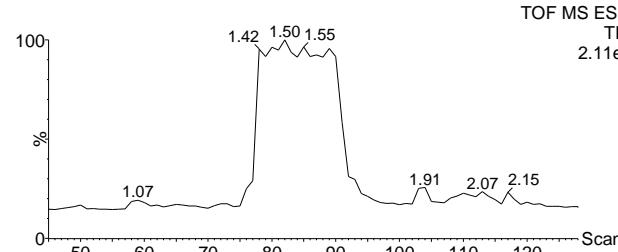


POLYESTER PU

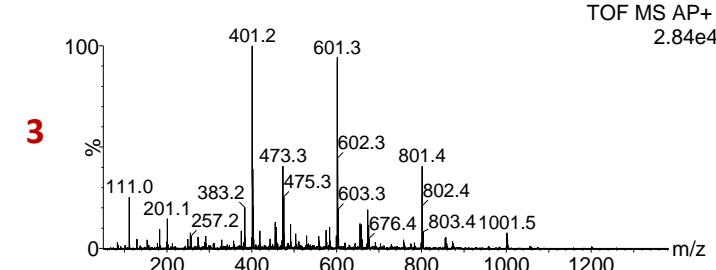
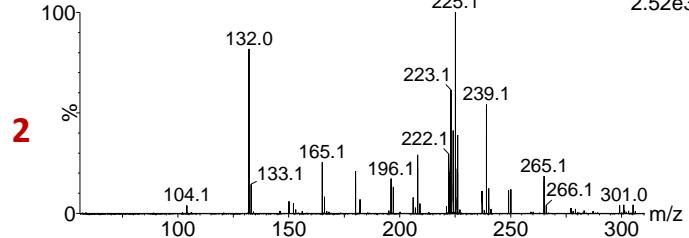
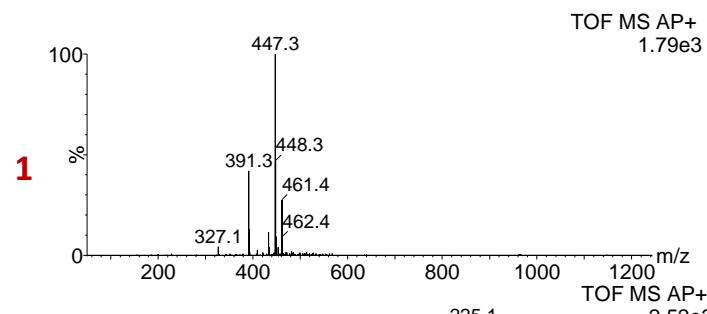
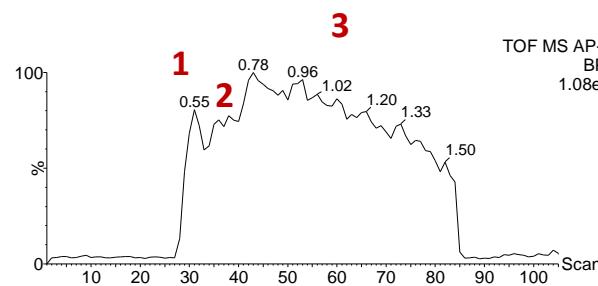
MS SPECTRA COMPARISON



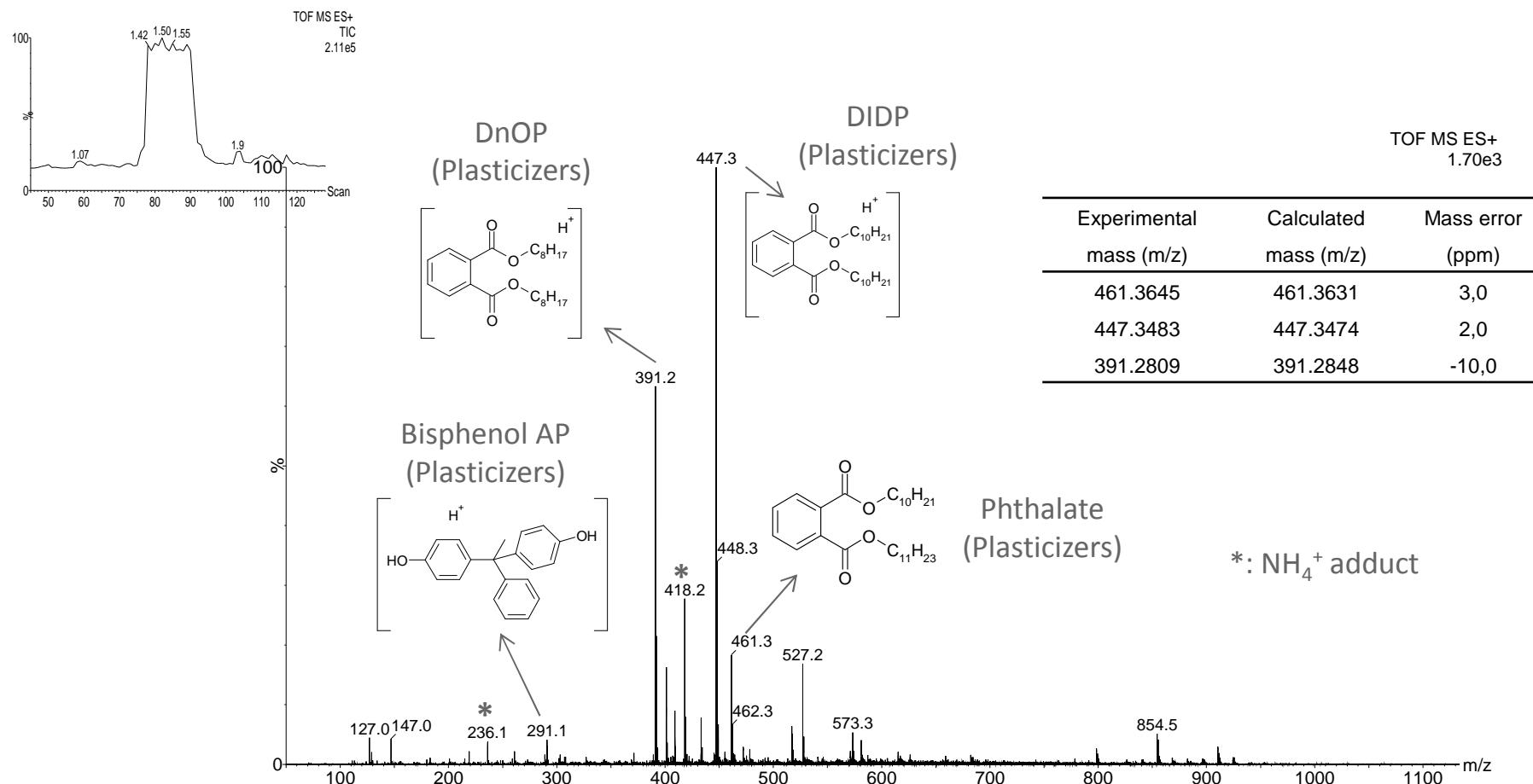
DART



ASAP

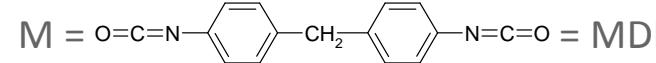
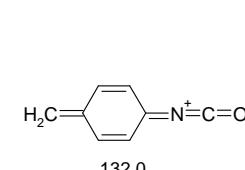
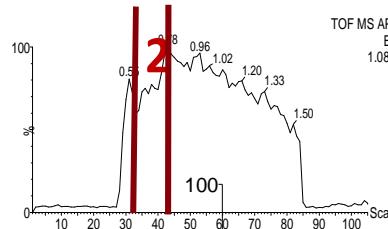


DART ANALYSIS – WIND SOCK

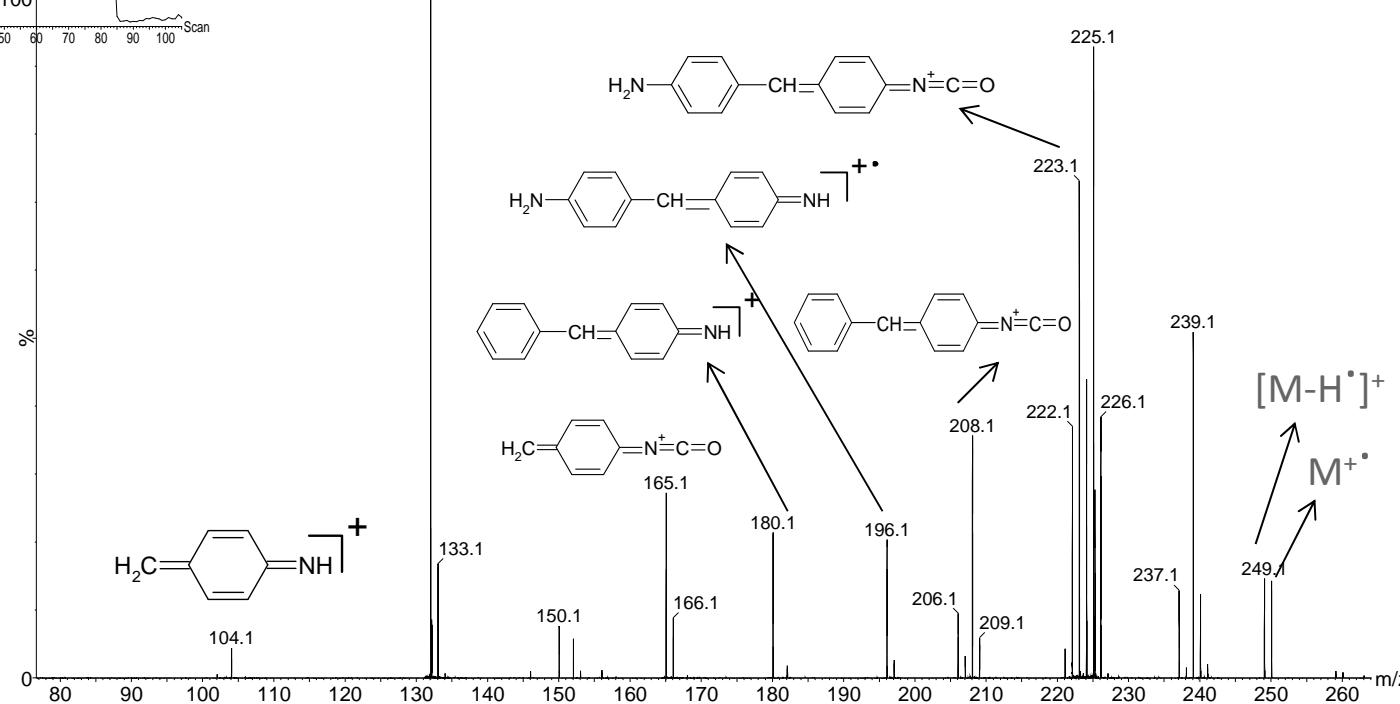


- No polymeric distribution
- TOF analyzer → exact mass measurements → additives identification
- Additives mass spectrum with good intensity and no in-source dissociation
- Similar mass spectrum as ASAP

ASAP ANALYSIS – WIND SOCK



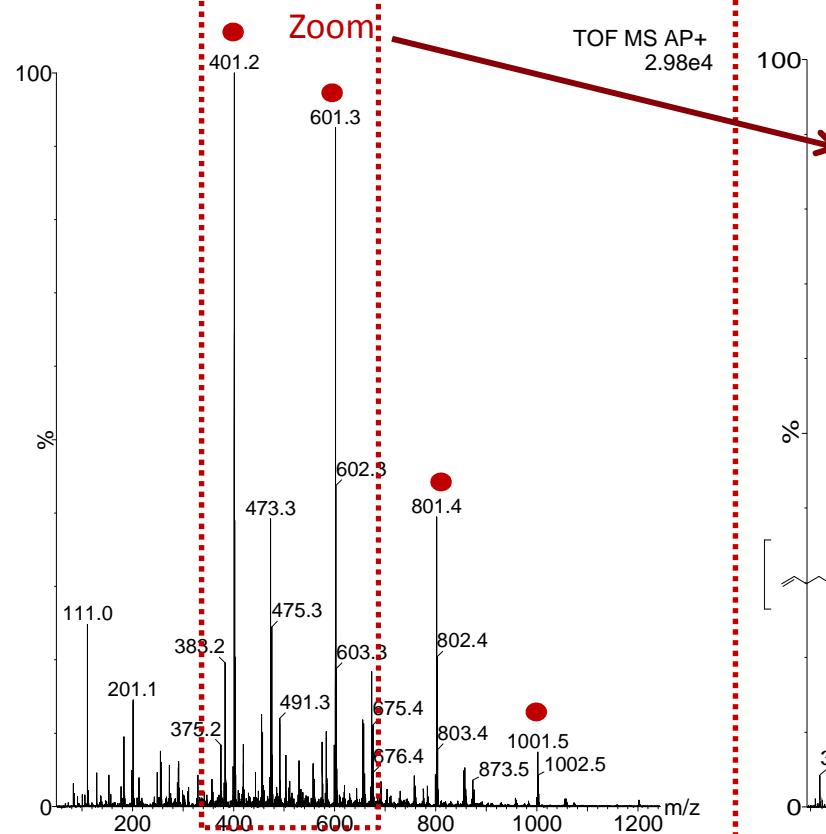
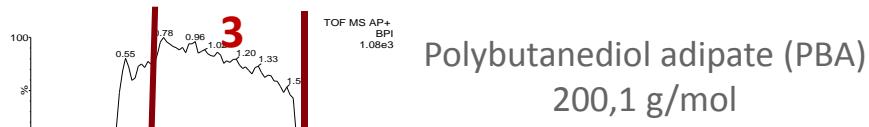
TOF MS AP+
1.91e3



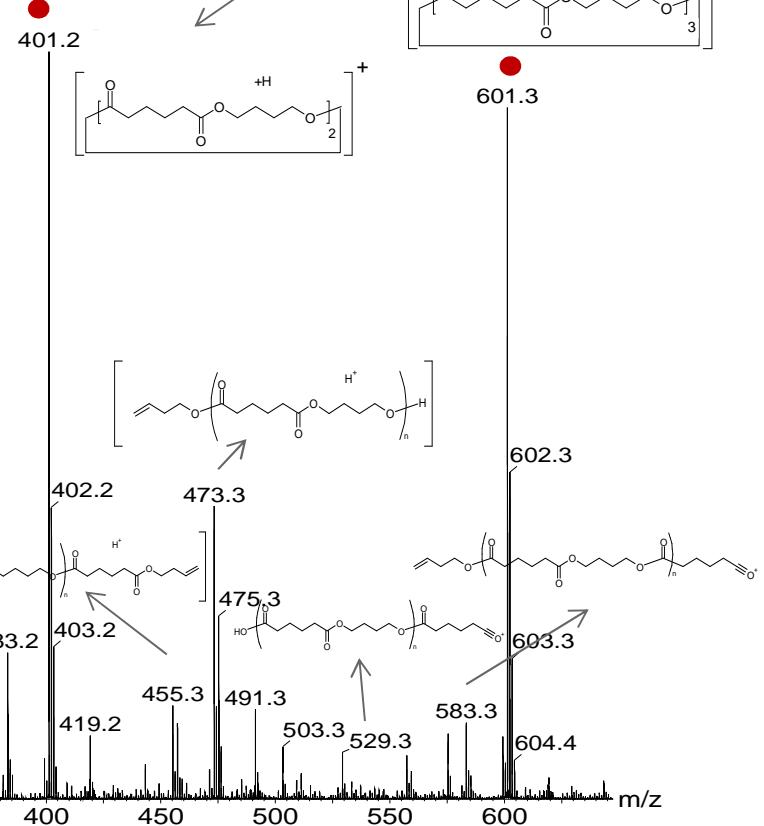
- Detection of molecular ion $\text{M}^{+\bullet}$ for MDI
- Detection of characteristic fragments of MDI: pyrolysis products and in-source dissociations:
 - 1,5 H transfert from β -CH or 1,3 H transfert from NH
 - Or radical abstraction

⇒ Structural identification of the PU Hard Segment

ASAP ANALYSIS – WIND SOCK



Lactonisation of polyesters with temperature

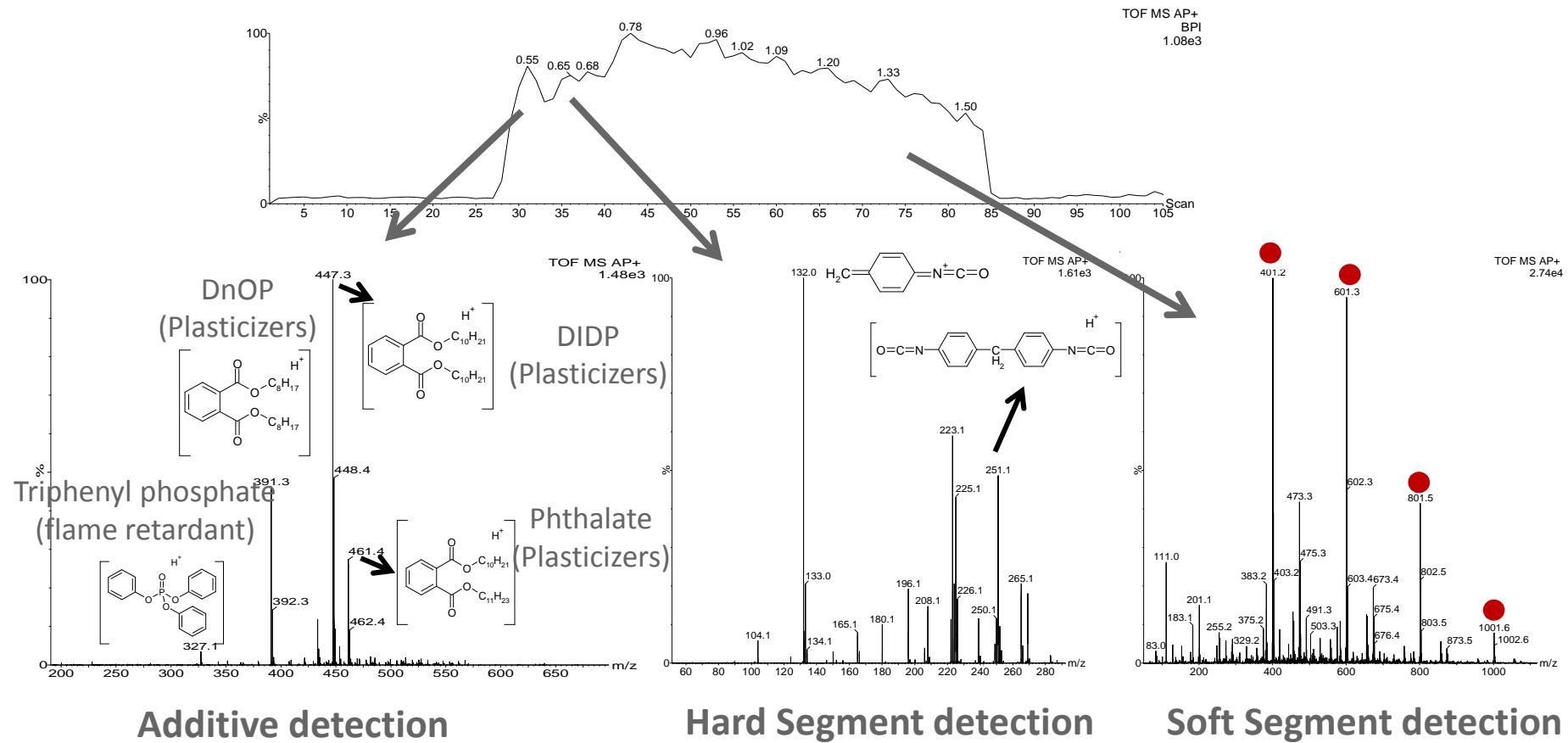


Fragments ions produced

- by pyrolysis degradation: intramolecular ester exchange → cyclic polyester
- supposed to be by low energy dissociation: 1,5-H transfer from β-CH

⇒ Structural identification of Soft Segment of PU

ASAP ANALYSIS - WIND SOCK



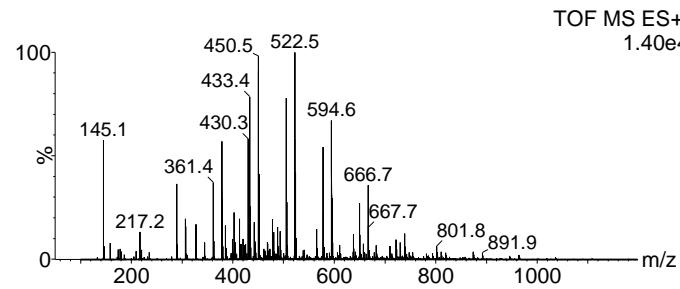
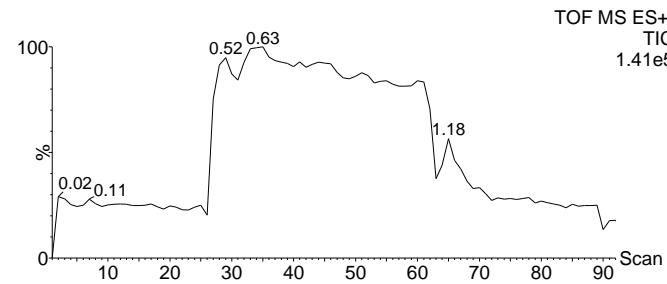
- Desorption of the components can be controlled by applying a gradient of temperature
- Additives are desorbed at lower temperature than segments of PU
- Hard segment is thermally degraded at lower temperature than soft segment → information on PU thermal sensibility (results confirmed by ATG experiments)

POLYETHER PU

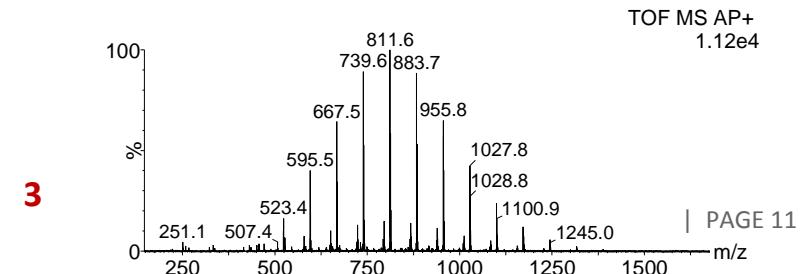
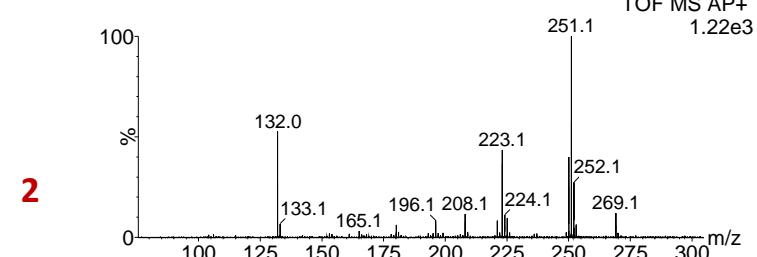
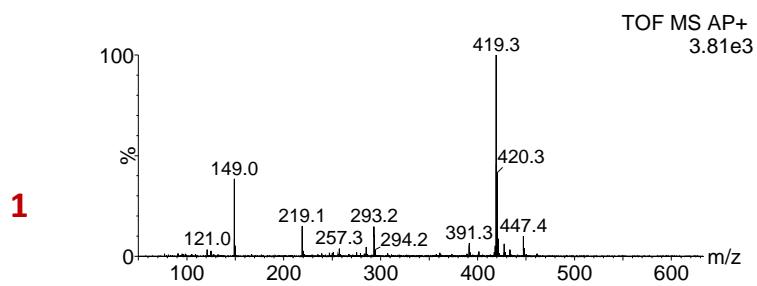
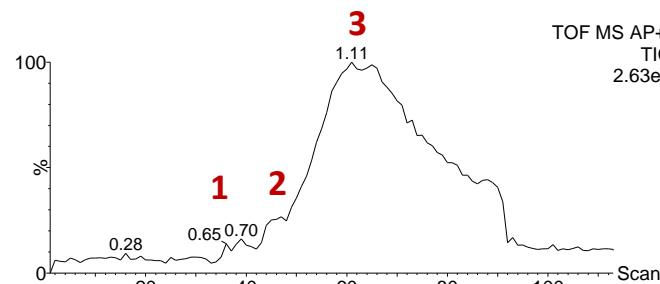
MS SPECTRA COMPARISON



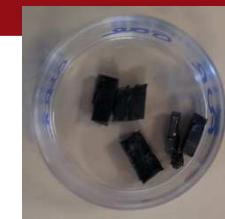
DART



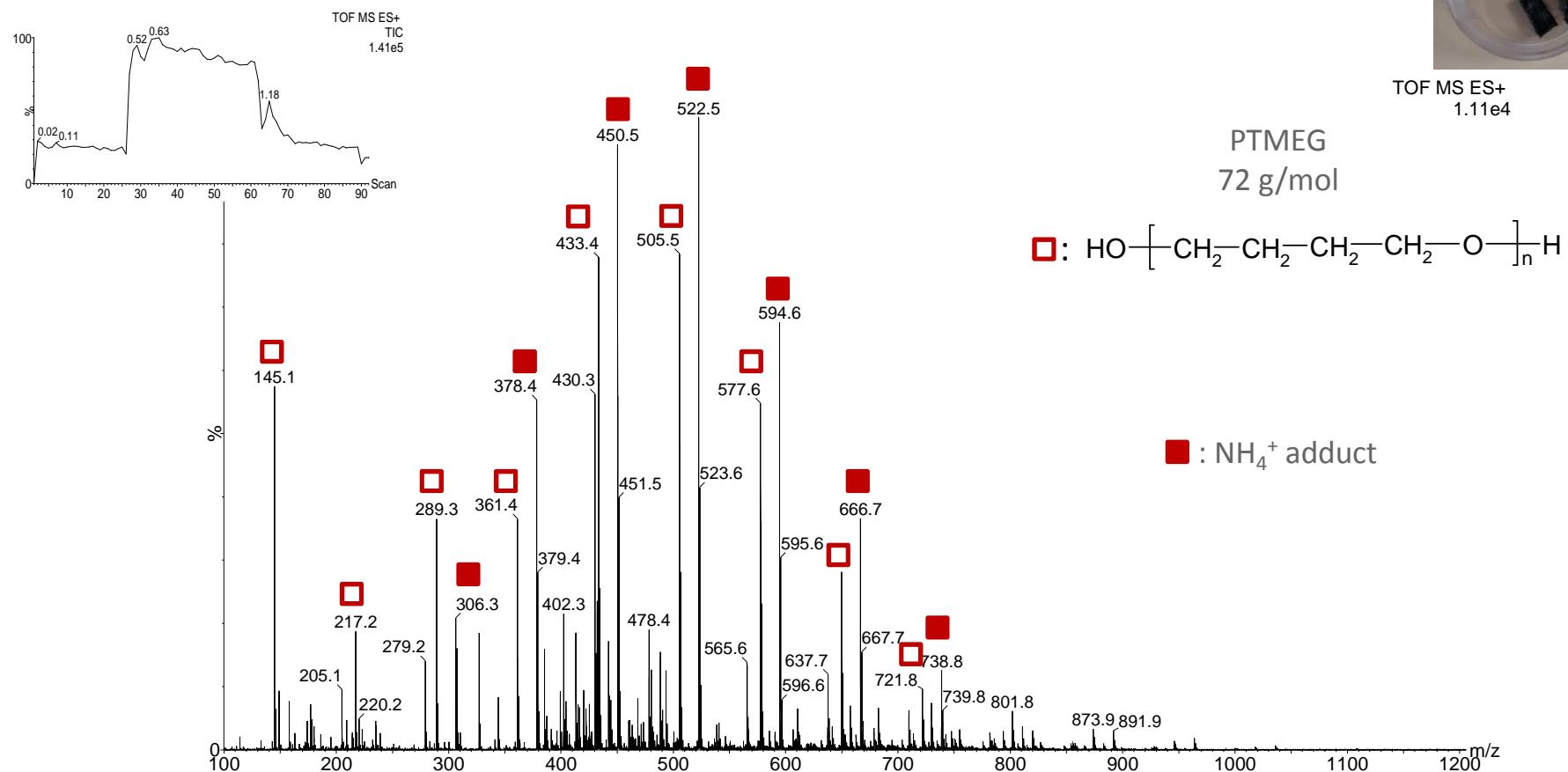
ASAP



PU POLYETHER - ELECTRIC CABLE SHEATH

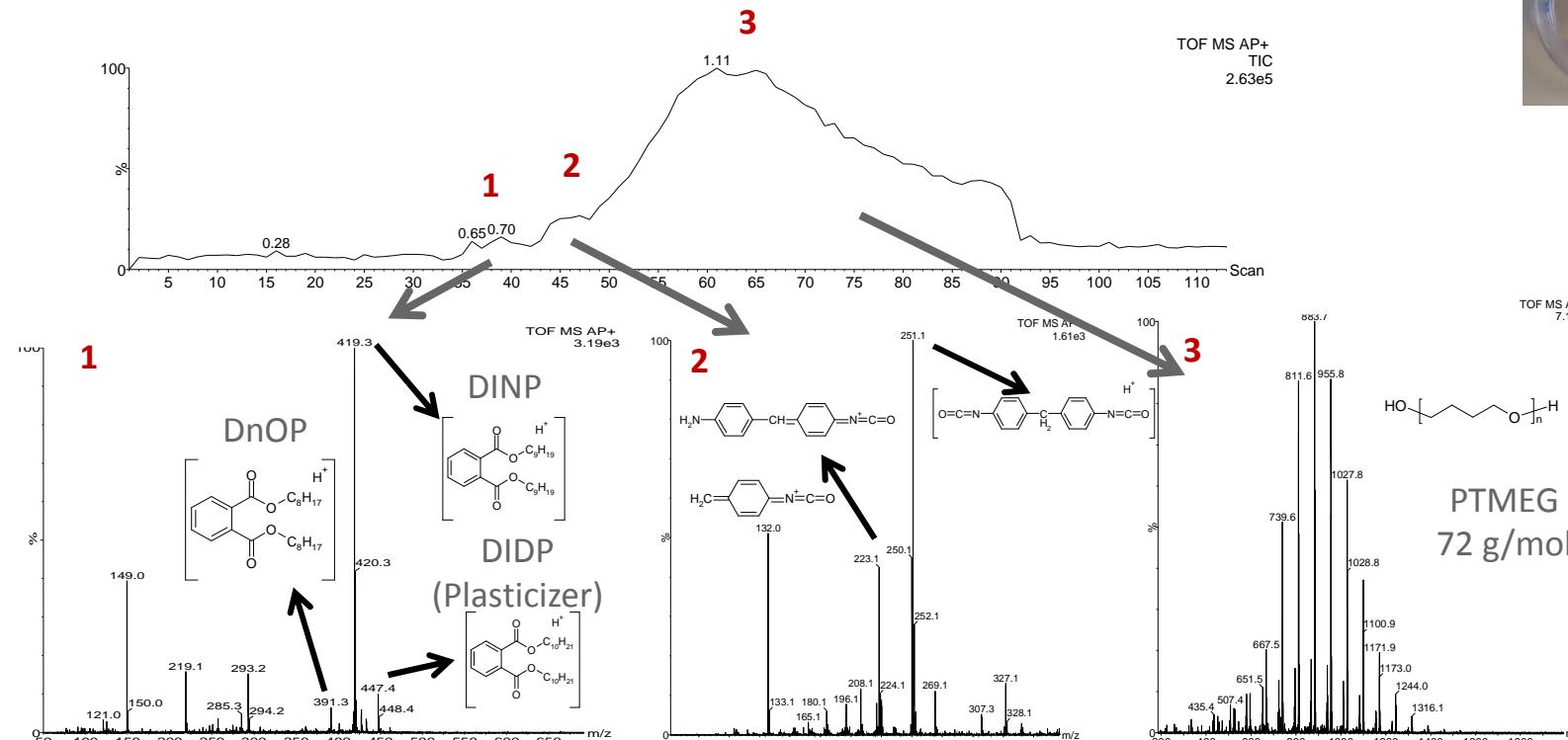


DART Analysis



- Detection of polyether polymer (PTMEG) → detection of soft segment
- Detection of ammonium adducts
- Polyether PU: only polymer detection and no information on additives

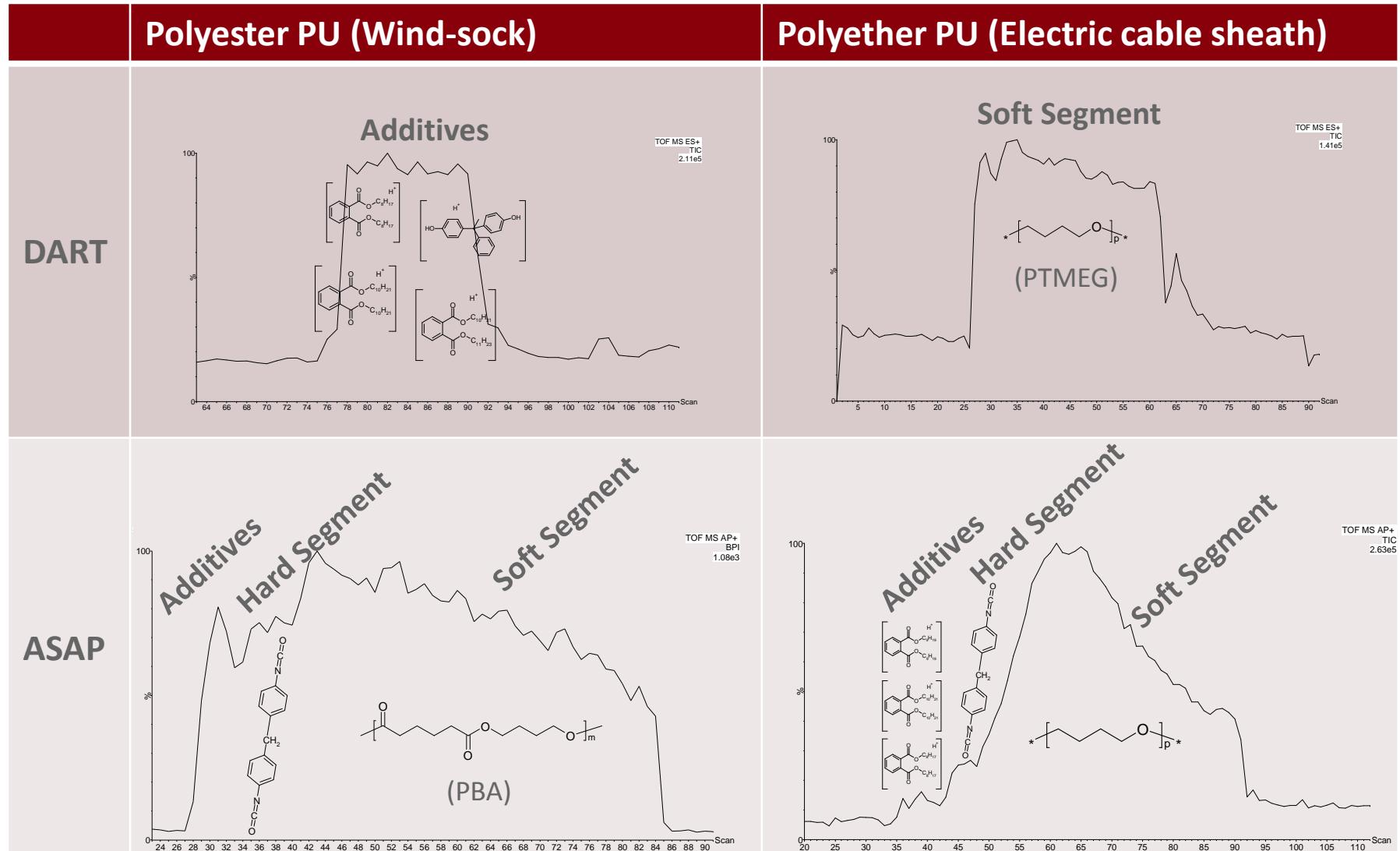
ASAP Analysis



- Desorption of the components controlled by the temperature
- Additives are desorbed at lower temperature than segments of PU
- Hard segment is thermally degraded at lower temperature than soft segment → whatever the soft segment nature, hard segment is more thermally sensible

CONCLUSIONS

COMPARISON OF POLYMERS ANALYSIS



CONCLUSIONS

COMPARISON OF ANALYTICAL TECHNIQUES

DART	ASAP
<p style="text-align: center;">Fast analysis (< 1 min) Two similar desorption/ionization processes</p>	
<ul style="list-style-type: none"> ■ No sample preparation ■ Less complicated mass spectra ■ Good sensitivity for additives detection ■ Detection of soft segment of polyether PU only 	<ul style="list-style-type: none"> ■ Characterization of the PU: Hard and soft segments (polyether and polyester) ■ Identification of additives ■ Fragment ions: <ul style="list-style-type: none"> ■ Pyrolysis products ■ In-source dissociation, resulting from C-C and C-O bonds cleavages (radical and charge directed process) ■ Desorption of compounds with gradient of temperature: <ul style="list-style-type: none"> ■ Temporal separation of molecules in function of their volatilization and/or degradation temperature ■ ASAP allows the study of thermal degradation of PU

⇒ Two complementary thermal-based ionization techniques for the study of crude polymer and their additives, directly on the sample

Thank you for your attention.

ACKNOWLEDGMENTS

Radiolysis group from LRMO

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U. Hohenester (CEA-Saclay, DSV)

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