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Identification and quantification of UV stabilizers in polymers by Pyrolysis GC Time-of-Flight Mass Spectrometry coupled with Size Exclusion Chromatography

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Introduction

The role of additives in polymers is very important for stabilization and functionalization. It provides additional properties to the polymer which add value for end-use application. Unknown UV stabilizers are difficult to identify in polymers due the presence of the polymeric matrix and also the often high molecular weight and low volatility of the compounds making them unsuitable for conventional capillary gas chromatography.

A novel on-line hyphenated methodology has been developed where size exclusion chromatography (SEC) in stopped flow mode was coupled with Pyrolysis Time-of-Flight Gas Chromatography Mass Spectrometry (Py-GC-TOFMS) through a commercially available sampling interface.[1],[2]
In the first step, oligomers and additives are separated from the polymer matrix in size exclusion mode using a low range molecular weight column. Fractions are taken on-line and passed through to a pyrolyzing GC injector. Pyrolyzed fragments are separated by GC and finally detected by high resolution TOFMS.

Experimental

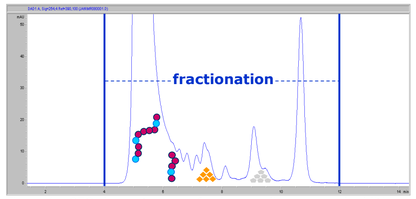


Figure 1: SEC chromatogram of polymer, oligomers and additives; the entire SEC chromatogram from 4-12 minutes is fractionated into multiple fractions (nominal 45µl) for pyrolysis-GC-TOFMS characterization.

Polymer | Polymer solution | SEC system | GC system | TOF-MS system

1. GPC separation (high resolution in the oligomeric region)
2. Fraction collection of SEC effluent (using stop flow mode)
3. LVI injection and solvent elimination step
4. Pyrolysis of retained polymer/oligomer and additive?
5. Cold trapping (LN_2) of decomposition products
6. Start GC separation of pyrolysis fragments by heating the trap
7. Ionization (EI) of individual compounds
8. Time-of-Flight MS detection (accurate mass)

Results

1. Fractionation and Identification fragments of UVA

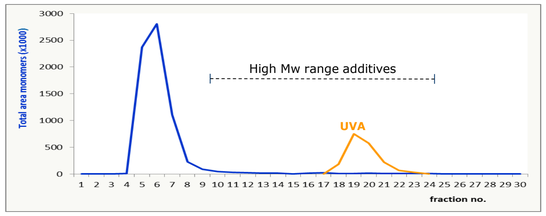


Figure 2: Characterization of a polymer; measured distribution of monomers versus UV absorber (fragments identified in fraction no. 18, 19, 20, 21, 22 and 23) by on-line SEC-Py-GC-TOFMS(EI).

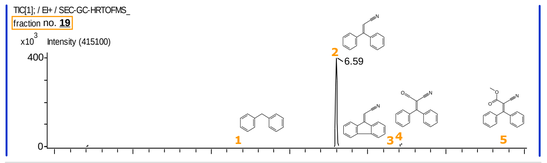
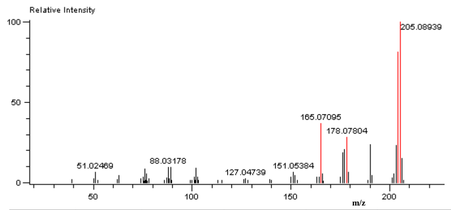


Figure 3: Total Ion Chromatogram (TIC) of one fraction analyzed by Py-GC-TOFMS. Identification done by library searching (NIST) or by high resolution (R > 6000) accurate mass measurement. Peaks: 1= diphenylmethane, 2= 3,3-diphenyl-2-propenenitrile, 3= 9-(cyanomethylene)fluorene, 4= diphenylacrylonitrile 2-carboxyaldehyde, 5= diphenyl-2-yl-cyano-acrylic acid methyl ester.

2. Accurate mass and Structure Elucidation UVA



Measured Mass	Calculated Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
205.08939	205.08915	0.24	1.18	$C_{15}H_{11}N$	11.0
204.08201	204.08132	0.68	3.36	$C_{15}H_{10}N$	11.5
178.07804	178.07825	-0.21	-1.17	$C_{14}H_{10}$	10.0
165.07095	165.07043	0.53	3.19	$C_{13}H_9$	9.5

Figure 4: EI mass spectrum of the main decomposition component (Retention time = 6.59/ figure 3) and estimated compositions of the major ions (red selected peaks) using elemental composition tool in JEOL MassCenter software.

The resulting molecular fragments after analytical pyrolysis gives information about the nature and identity of the original larger molecule.

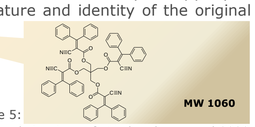


Figure 5: Chemical structure of UV absorber Uvinul 3030

3. Calibration and quantification of high Mw UVA

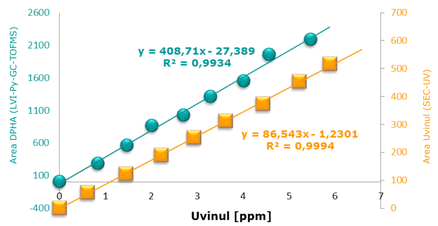


Figure 6: Calibration curve for Uvinul 3030 (range 0-6 ppm) determined by SEC-UV (orange dotted line). In case of low or non-UV sensitive compounds, calibration can be performed using LVI-Py-GC-TOFMS (green dotted line).

Calculation steps in quantification of UVA loading by SEC-UV:

* Standard Error of Calibration (SEC) = 0.052 ppm
* Predicted Quantification Limit for Uvinul 3030 in a polymer sample [99.7% confidence interval] = 0.0046 wt% = 46 mg/kg = 46 µg/g
* Average amount of Uvinul in polymer [n= 5; sample prep] = 0.12 wt%
* Sample Standard Deviation (s) = 0.00031 wt%
* Coefficient of Variation (CV)= $\frac{S}{\bar{X}}$ = 0.0025

Note: Relative Standard Deviation = 100 x CV

Conclusions

•This optimized analytical methodology can be used for fast screening and quantification of high molecular weight UV absorbers in polymers.

•Method is also applicable for other additives (like heat-stabilizers, anti-oxidants, release agents) and branching studies as well for monomer and end-cap identification.

•Combination with TOFMS enables precise identification of compounds by providing elemental formulas based on accurate mass for every peak.

•The hyphenated system can also be used for chemical composition measurements for complex copolymers as function of the Mw.

References/ Acknowledgements

[1] E.R. Kaal et al., J.Chromatogr. A *1143,* 182-189(2007)
[2] ATAS GL International B.V., Eindhoven (NL)

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