LIQUID CHROMATOGRAPHY FOR SUTAINABLE QUALITY CONTROL AND PRODUCT DEVELOPMENT

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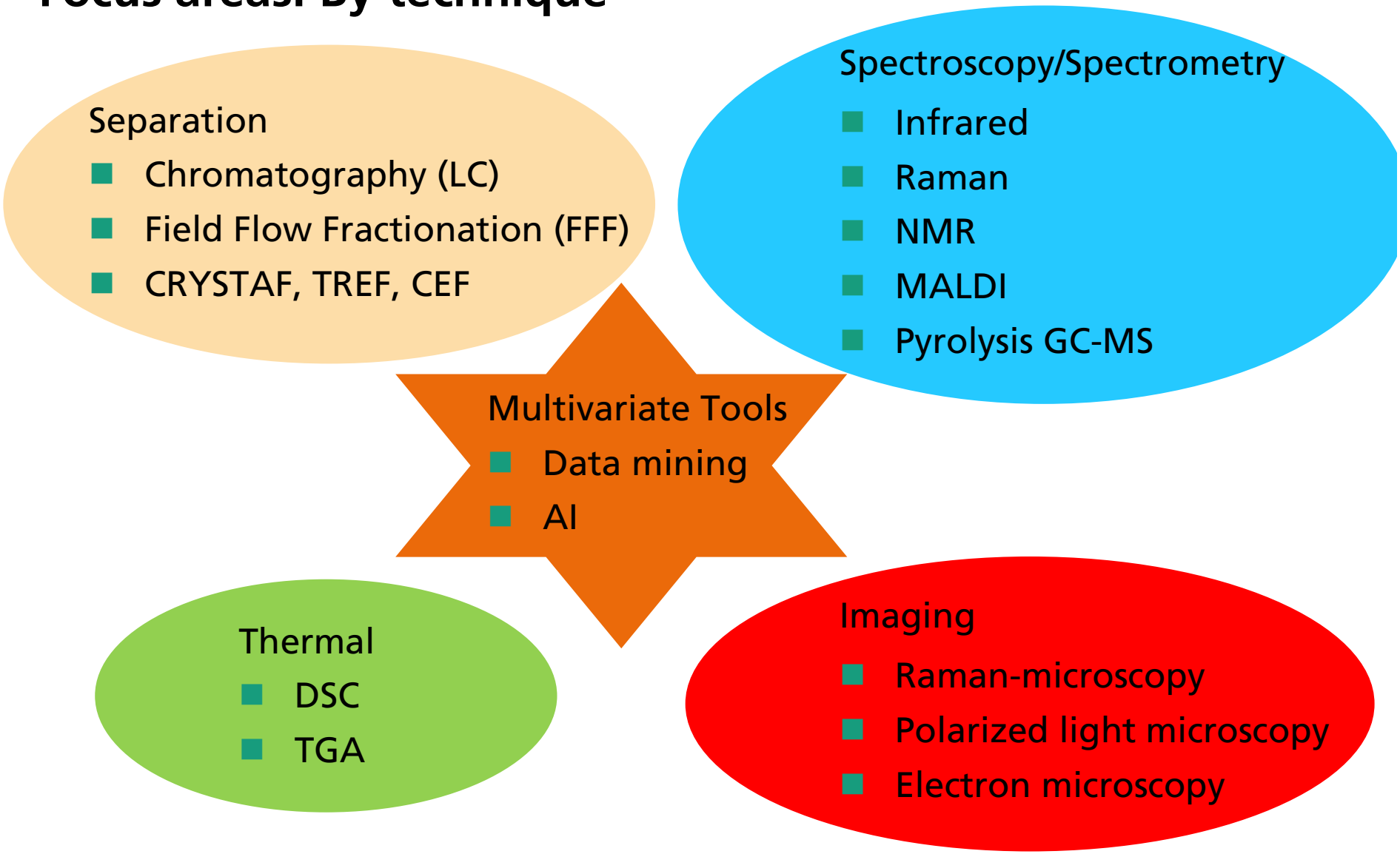
Focus areas: By technique



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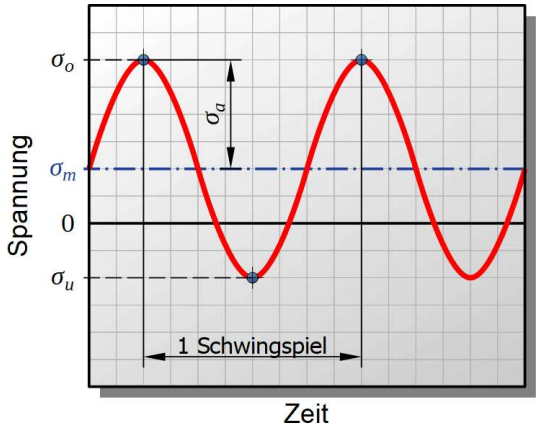
Developing analytical methods for

Recyclates

Biobased polymers and additives



Evidence based testing and failure analysis

Sustainable polymer production and compounding

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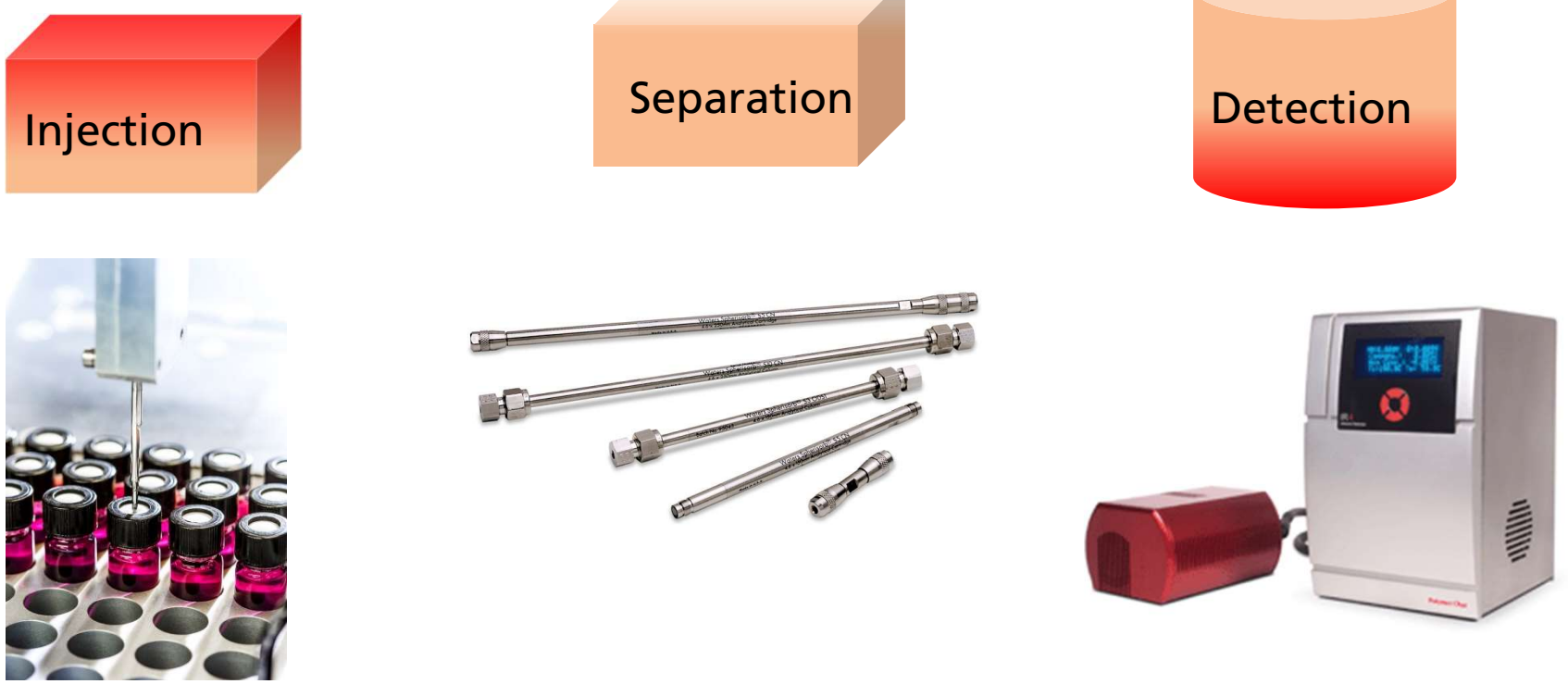
Liquid Chromatography – the workhorse to characterize Thermoplastics



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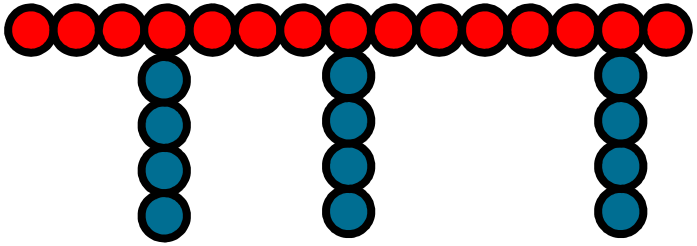
Blockcopolymer

Altenierendes Copolymer

statistisches Copolymer

Gradientencopolymer



Pfropfcopolymer

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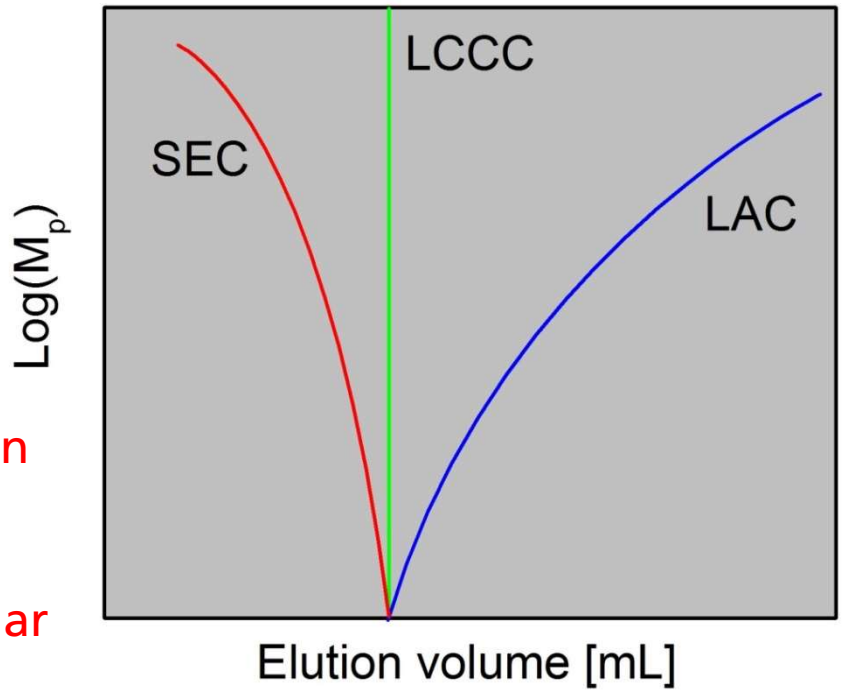
Separation modes in liquid chromatography of polymers

- **Size Exclusion Chromatography (SEC)**
- **Liquid Adsorption Chromatography (LAC)**
- **Liquid Chromatography at Critical Conditions (LCCC)**



LCCC → Elution volume is **constant** for macromolecules with different molar masses.

SEC → Elution volume **decreases** with the molar mass.

LAC → Elution volume **increases** with the molar mass.

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Detection: the Key to Information

Information gained	IR	RI	NMR	MALS	UV	ELSD
Concentration	+	+	+	-	+	-
Composition	+	-	+	-	+	-
Structure	-	-	+	+	-	-
Calibration	-	-	+	+	-	-
Solvent Requirement	yy	y	yy	yy	y	n

- **Almost as a rule, multidetection is needed**

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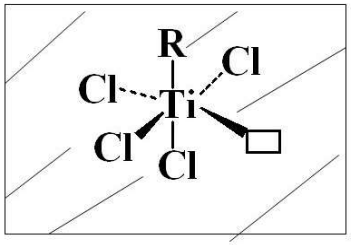
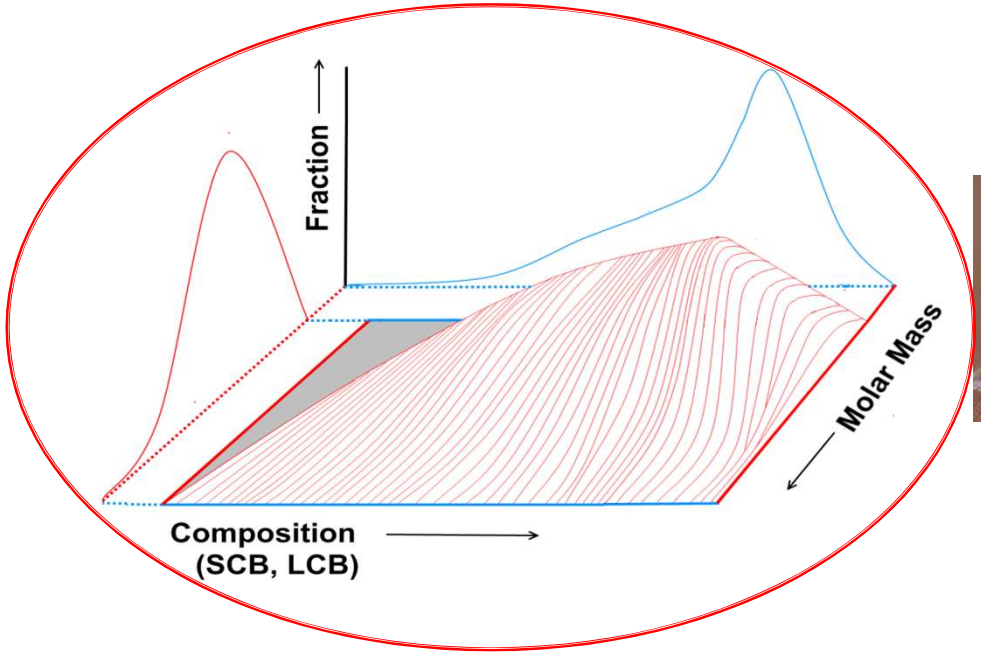
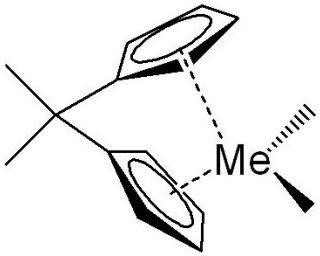
The Polymer DNA







- Molecular weight distribution (**MWD**)
- Chemical composition distribution (**CCD**)
- Stereochemical distribution
- Comonomer sequence length distribution
- Long chain branch distribution (LCB)

- Multidimensional techniques are required to analyze the chemical heterogeneity

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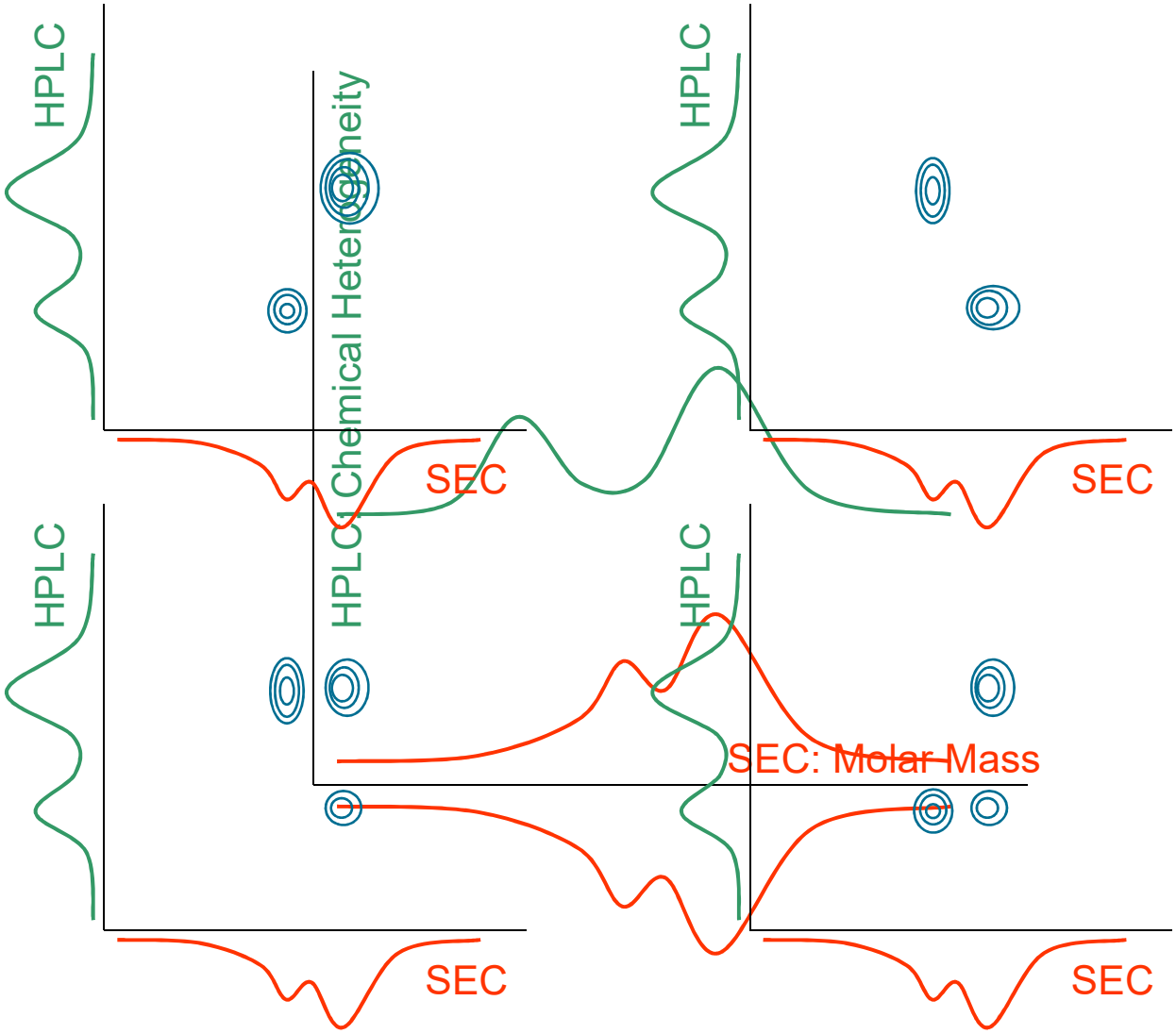
Why 2D LC????



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Graphite – Structure Selective Stationary Phase

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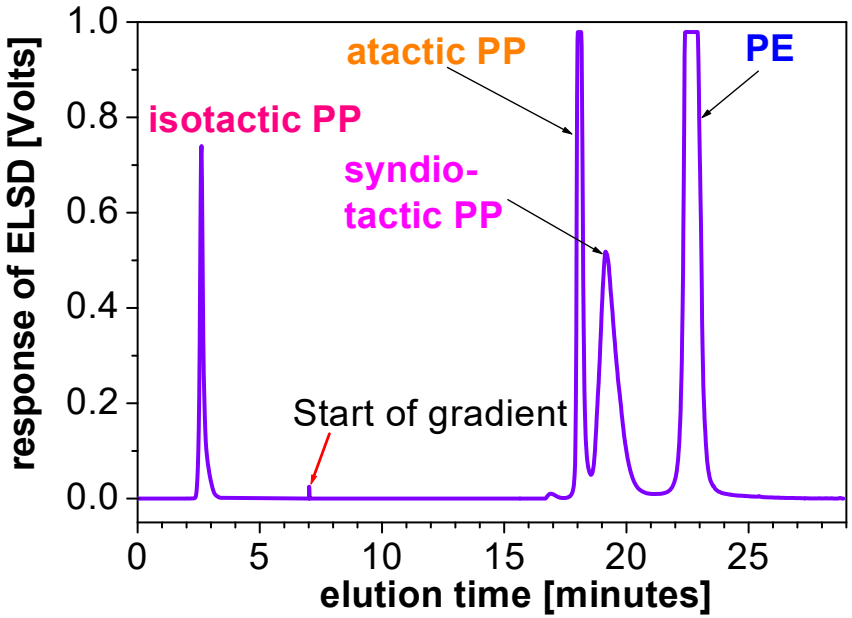
The Breakthrough



Stationary Phase: Hypercarb™
Mobile Phase: Decanol→TCB

- **Separation according to composition and microstructure is possible**

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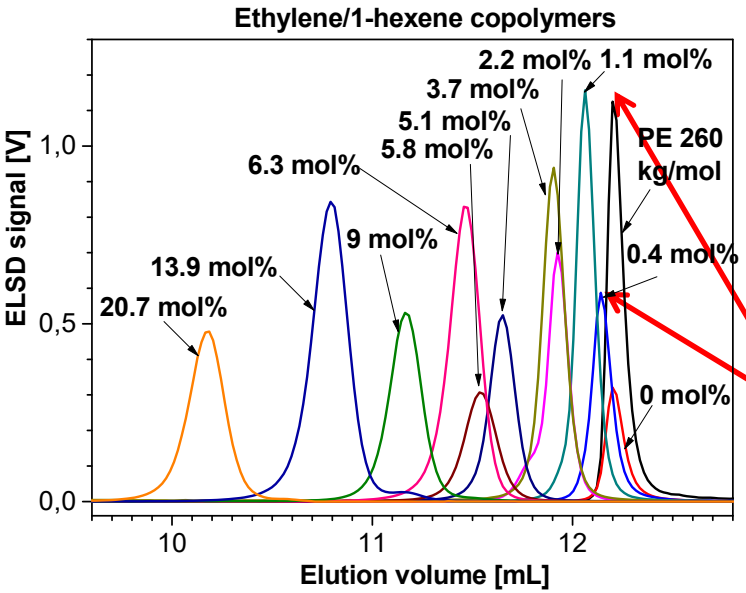
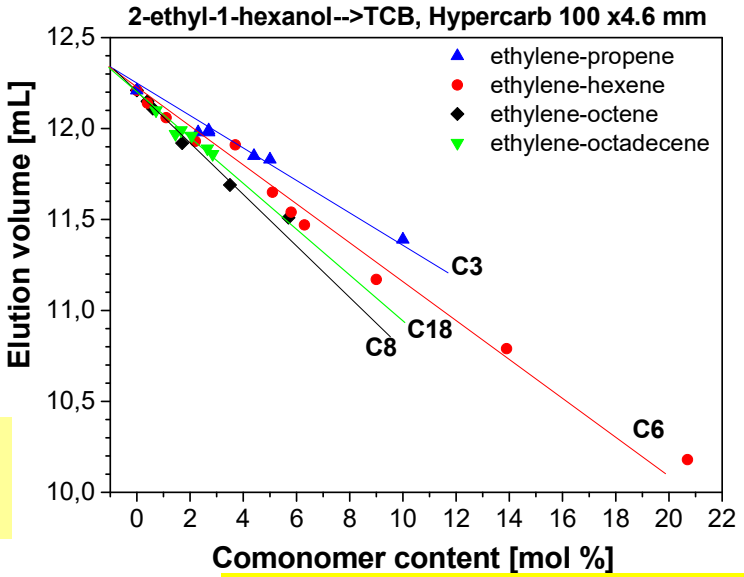
Solvent gradient interactive chromatography
Separation of LLDPE



Difference 0.4 mol %!



Linear dependence between the elution volume and the content of 1-alkene

Separation according to **length** and **short chain branching content**

Hypercarb, 2-ethyl-1-hexanol→TCB, 160 °C

R. Chitta, T. Macko, R. Brüll, Ch. Boisson, E. Cossoul, O. Boyron, Macromol. Chem. & Phys. 2015, 216, 721

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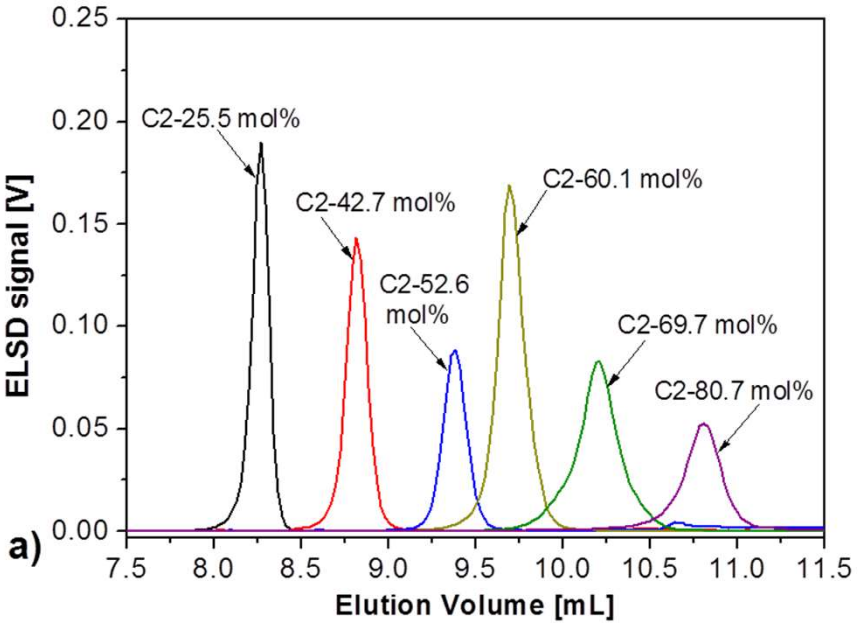
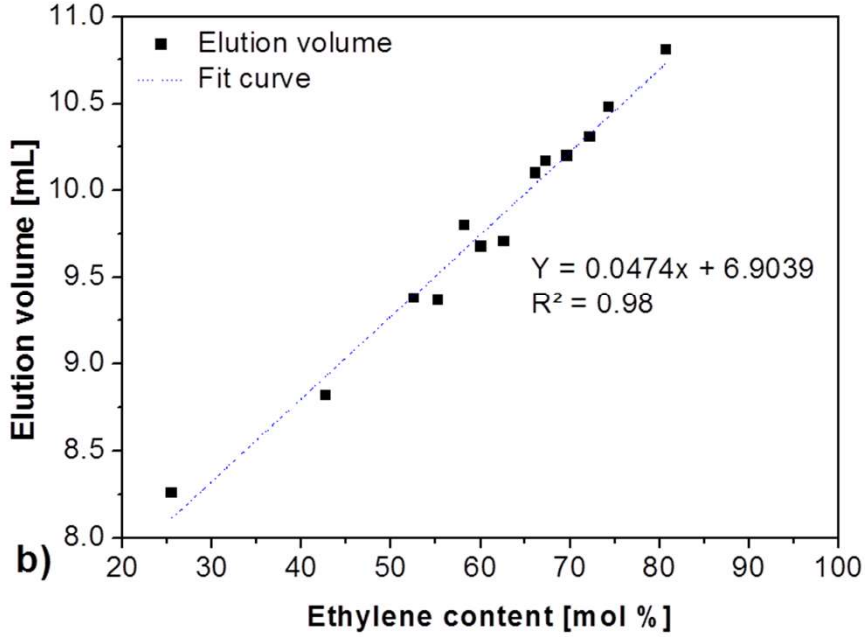
Separation of EP rubbers using HT-LAC





160 °C, Hypercarb™ & 1-decanol→TCB gradient (10 min)

- **Amorphous polymers can be analysed wrt composition distribution**

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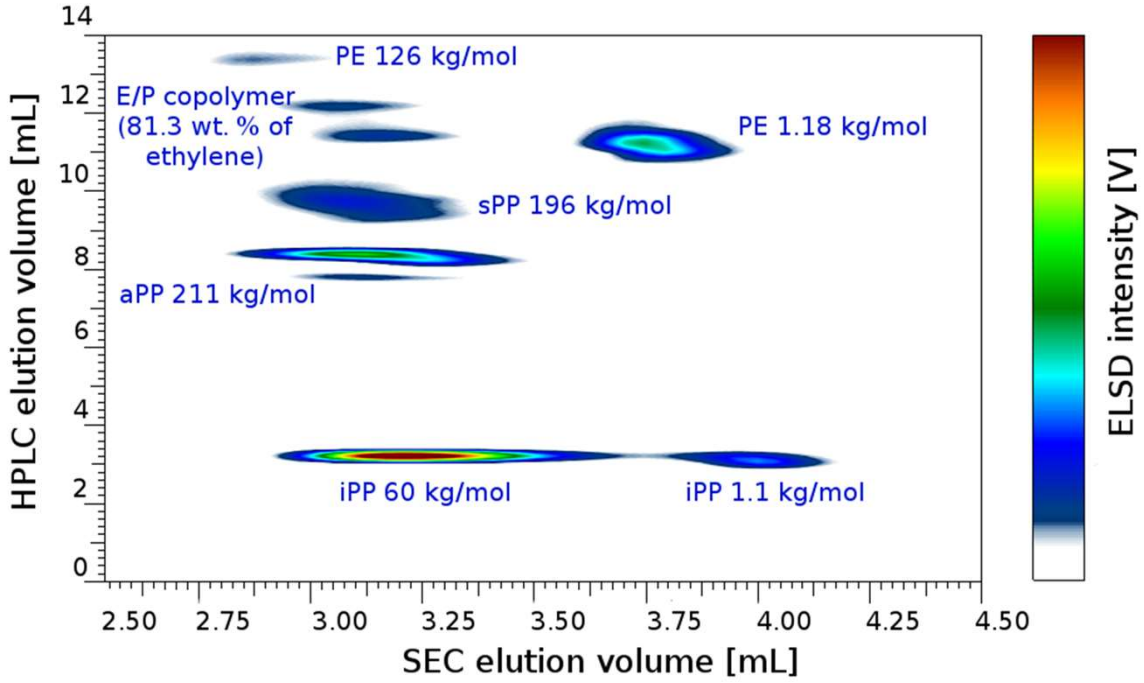
HT 2D-LC



HPLC: Hypercarb™, 1-decanol → TCB, 0.1 mL/min, 140 °C

SEC: PL Rapide™ H, TCB, 2.5 mL/min, 160 °C

- Highly complex mixtures can be comprehensively analyzed

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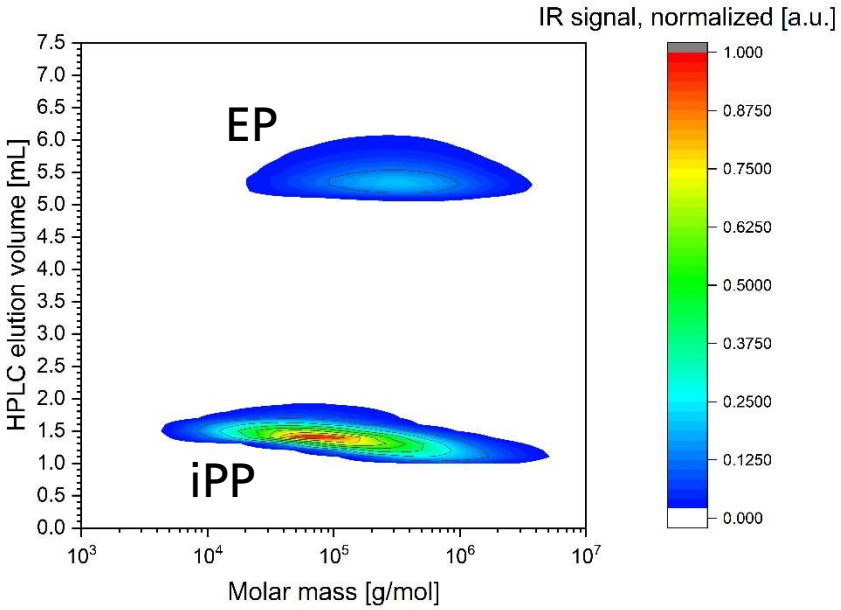
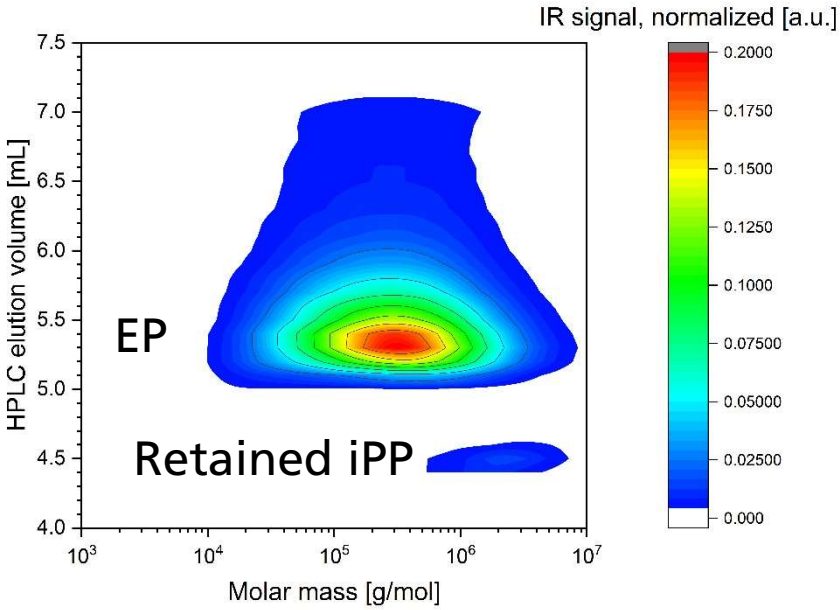
Appl. 1: 2D-LC-IR of PP with IR6

Overview



Zoom of retained part



- Same HIPP sample but NO prefractionation, ~ 8 mg/mL injected
  - HPLC gradient slightly adjusted (→ different elution times)

→ Excellent SNR (even retained iPP clearly identifyable)

→ Full extent of molar mass distribution apparent

→ Absolutely no need for prefractionation

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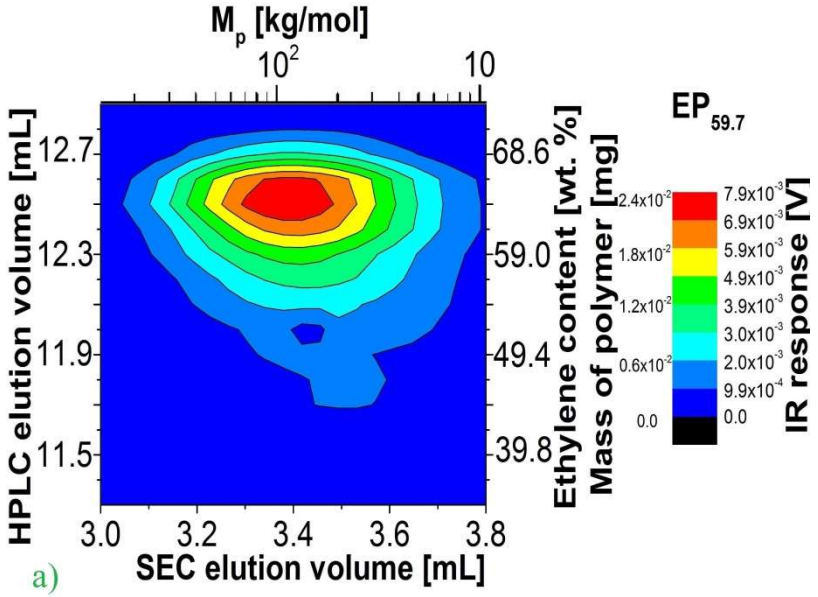
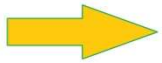
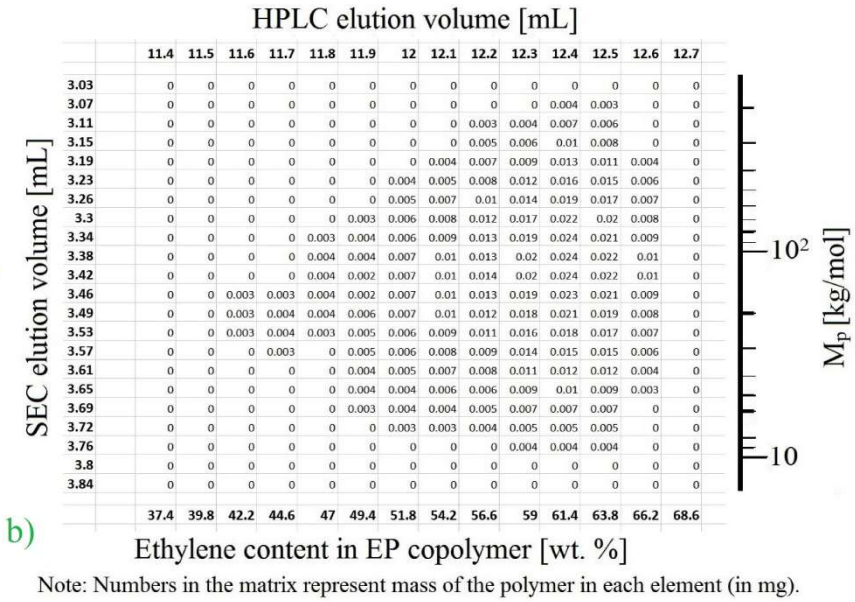
Matrix approach for quantification







	11.4	11.5	11.6	11.7	11.8	11.9	12	12.1	12.2	12.3	12.4	12.5	12.6	12.7
3.03	0	0	0	0	0	0	0	0	0	0	0	0	0	0
3.07	0	0	0	0	0	0	0	0	0	0	0.004	0.003	0	0
3.11	0	0	0	0	0	0	0	0	0.003	0.004	0.007	0.006	0	0
3.15	0	0	0	0	0	0	0	0	0.005	0.006	0.01	0.008	0	0
3.19	0	0	0	0	0	0	0	0.004	0.007	0.009	0.013	0.011	0.004	0
3.23	0	0	0	0	0	0	0.004	0.005	0.008	0.012	0.016	0.015	0.006	0
3.26	0	0	0	0	0	0	0.005	0.007	0.01	0.014	0.019	0.017	0.007	0
3.3	0	0	0	0	0	0.003	0.006	0.008	0.012	0.017	0.022	0.02	0.008	0
3.34	0	0	0	0	0.003	0.004	0.006	0.009	0.013	0.019	0.024	0.021	0.009	0
3.38	0	0	0	0	0.004	0.004	0.007	0.01	0.013	0.02	0.024	0.022	0.01	0
3.42	0	0	0	0	0.004	0.002	0.007	0.01	0.014	0.02	0.024	0.022	0.01	0
3.46	0	0	0.003	0.003	0.004	0.002	0.007	0.01	0.013	0.019	0.023	0.021	0.009	0
3.49	0	0	0.003	0.004	0.004	0.006	0.007	0.01	0.012	0.018	0.021	0.019	0.008	0
3.53	0	0	0.003	0.004	0.003	0.005	0.006	0.009	0.011	0.016	0.018	0.017	0.007	0
3.57	0	0	0	0.003	0	0.005	0.006	0.008	0.009	0.014	0.015	0.015	0.006	0
3.61	0	0	0	0	0	0.004	0.005	0.007	0.008	0.011	0.012	0.012	0.004	0
3.65	0	0	0	0	0	0.004	0.004	0.006	0.006	0.009	0.01	0.009	0.003	0
3.69	0	0	0	0	0	0.003	0.004	0.004	0.005	0.007	0.007	0.007	0	0
3.72	0	0	0	0	0	0	0.003	0.003	0.004	0.005	0.005	0.005	0	0
3.76	0	0	0	0	0	0	0	0	0	0.004	0.004	0.004	0	0
3.8	0	0	0	0	0	0	0	0	0	0	0	0	0	0
3.84	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	37.4	39.8	42.2	44.6	47	49.4	51.8	54.2	56.6	59	61.4	63.8	66.2	68.6

Note: Numbers in the matrix represent mass of the polymer in each element (in mg).

- Data base can be build
- Systematic development of structure-process-property relationships based on analytical evidence

S.S. Bhati, T. Macko, R. Brüll, Polyolefins J, 3, 2016, 119.

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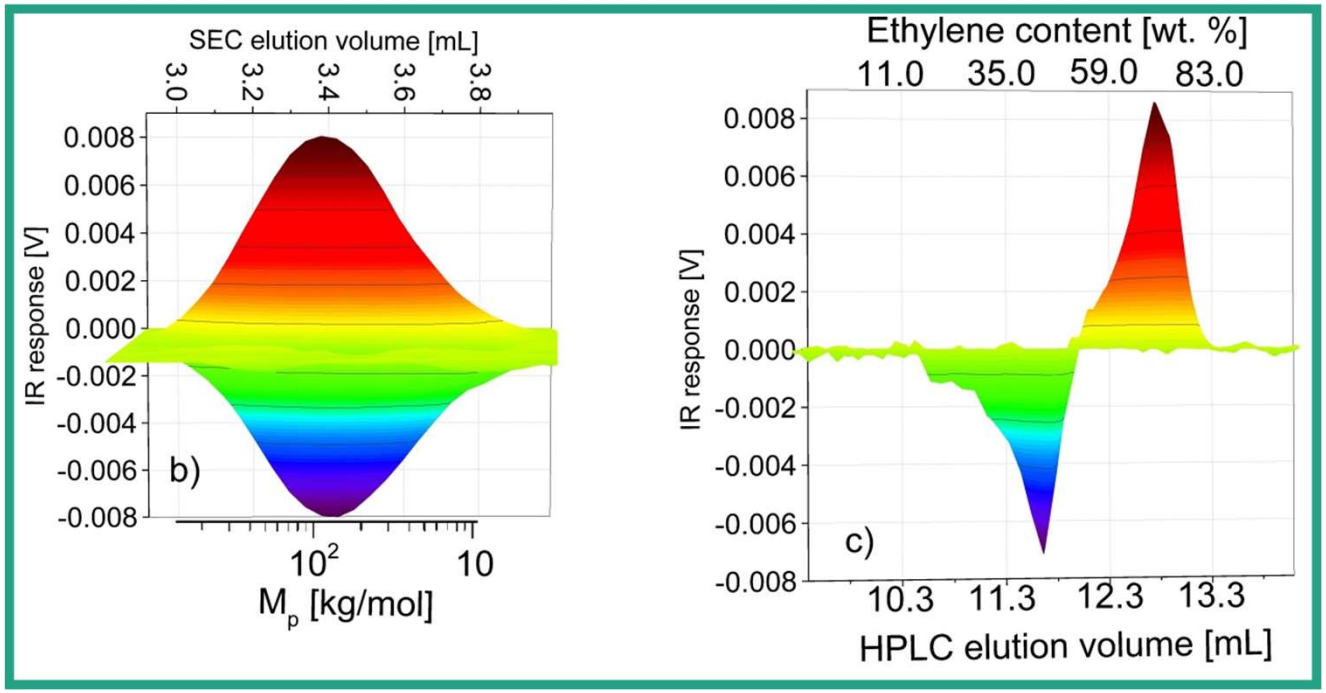
Quantifying unique segments in two copolymers



- Subtraction of Matrix $EP_{59.7}$ – Matrix $EP_{39.8}$ was used to create the three dimensional surface plots showing unique segments in both the copolymers and their MMD as well as CCD.
- Differences between samples can be quantified with the data from matrices.
- 89.5 wt. % unique segments

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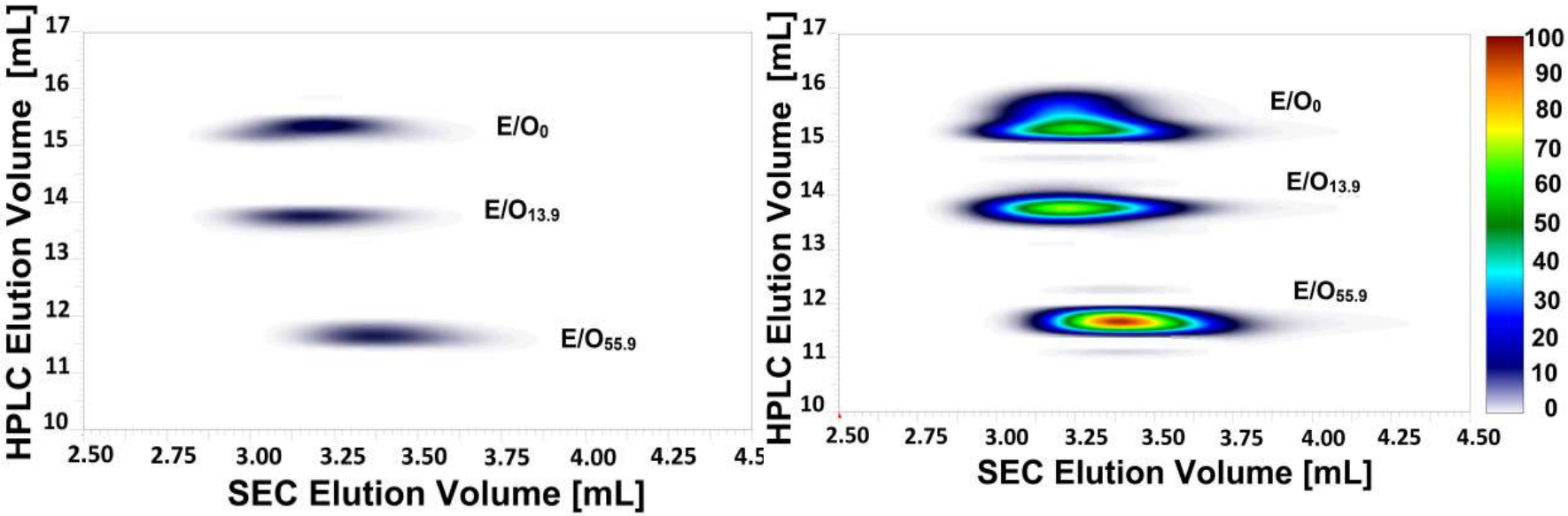
Improving Signal to Noise in HT 2D-LC



- Multiple injections increase signal intensity
- No shift in spot position

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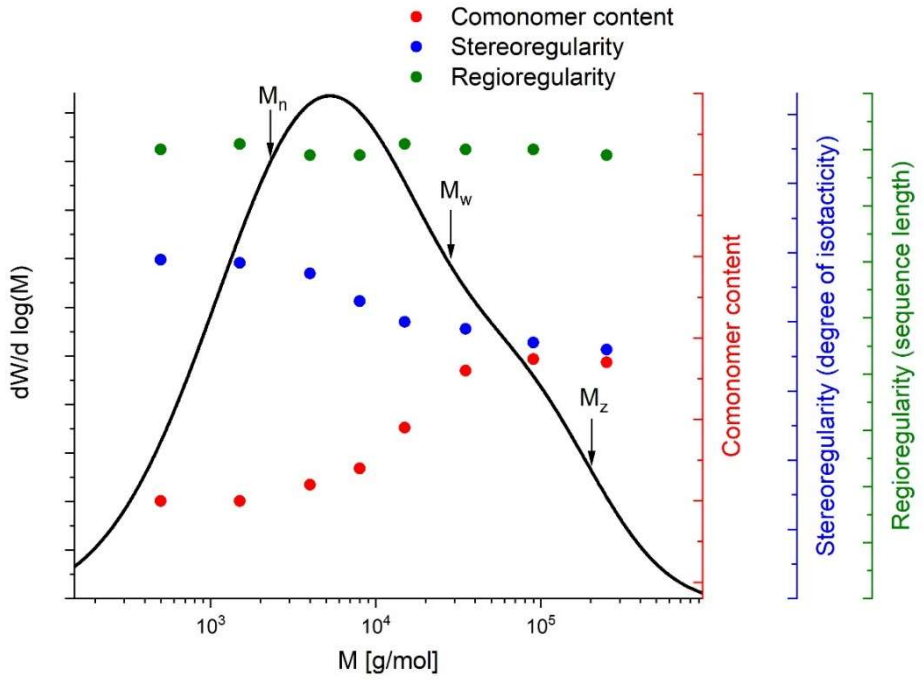
Fitting PP for new Applications

2019

2020



- Microstructure can be profiled as function of molar mass

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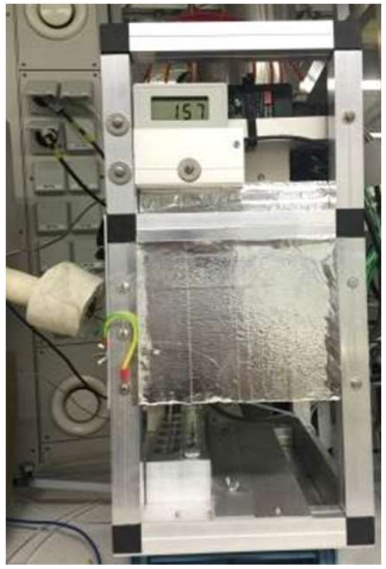
Preparative Liquid Chromatography



- Collect fractions from HPLC/GPC/2D-LC
- Workup (10 – 100 mg)
- NMR, DSC

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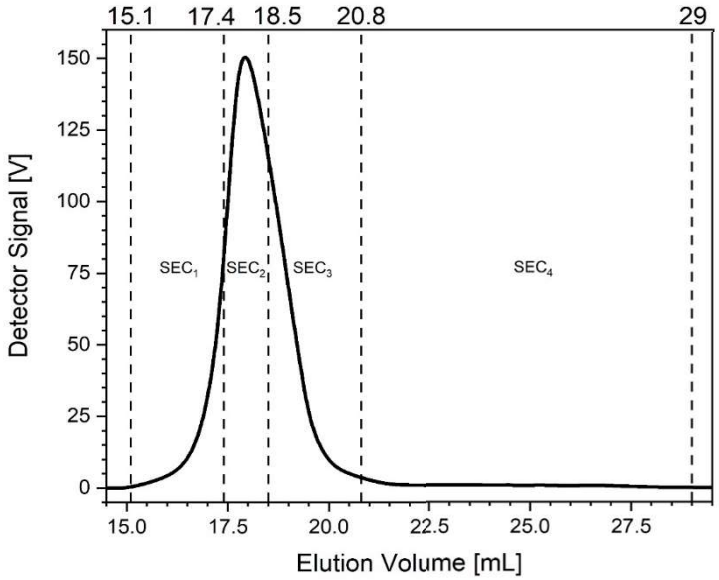
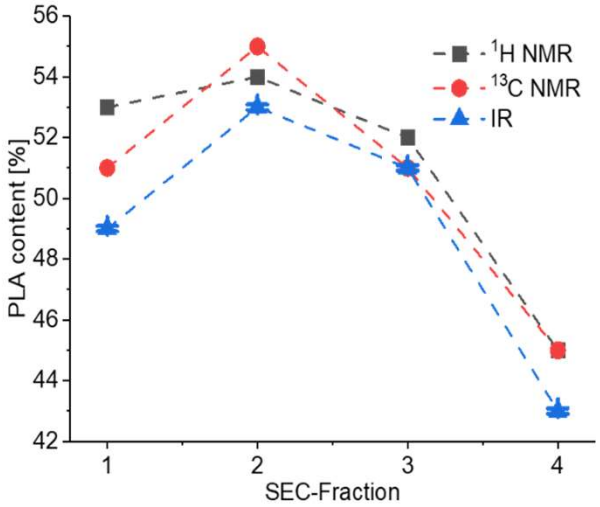
Appl. 2: LC-NMR of PLA/PBSA





- NMR delivers absolute value for composition, and trends correlate well with IR

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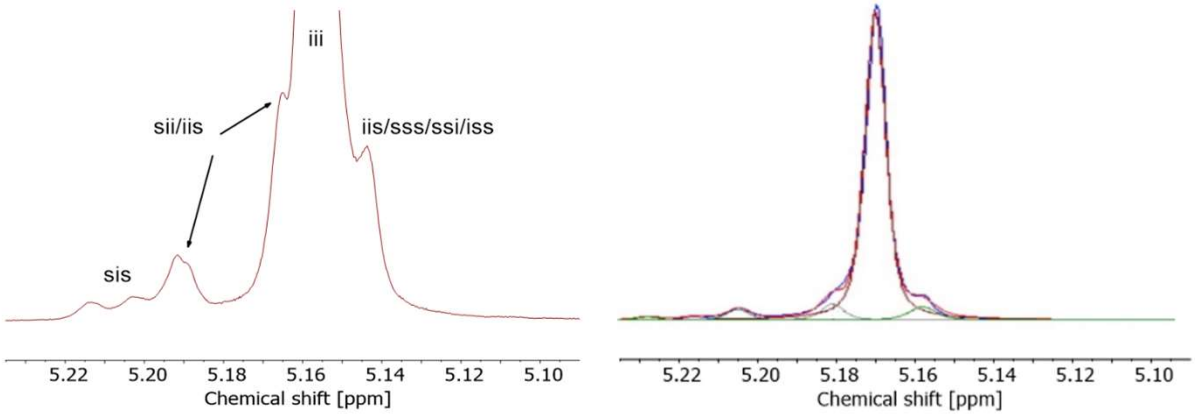
Appl. 2: LC-NMR of PLA/PBSA



	diads [wt%]			
	sis	sii/iis	iii	isi/sss/ssi/iss
Fraction C-SEC$_1$	4	6	81	8
Fraction C-SEC$_2$	1	3	88	7
Fraction C-SEC$_3$	2	4	87	7
Fraction C-SEC$_4$	2	4	86	6

	c(SBS) [wt%]	c(SBA) [wt%]	c(ABA) [wt%]	L(BS)	L(BA)	R
C-SEC$_1$	71	21	8	4.45	1.40	0.93
C-SEC$_2$	66	24	9	3.72	1.37	0.99
C-SEC$_3$	69	26	6	3.70	1.22	1.09
C-SEC$_4$	72	21	7	4.42	1.31	0.99

- Regio- and stereomicrostructure can be mapped

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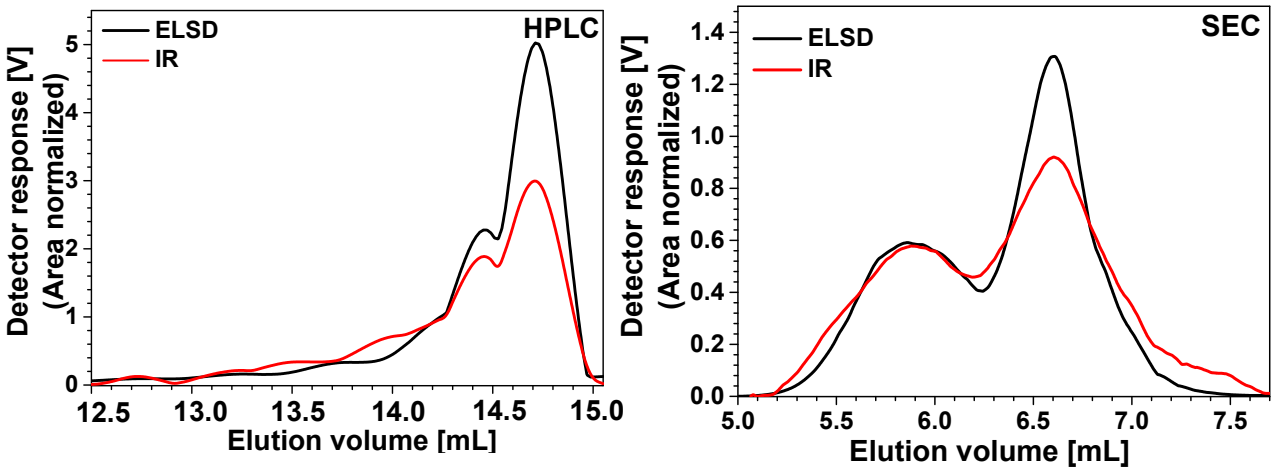
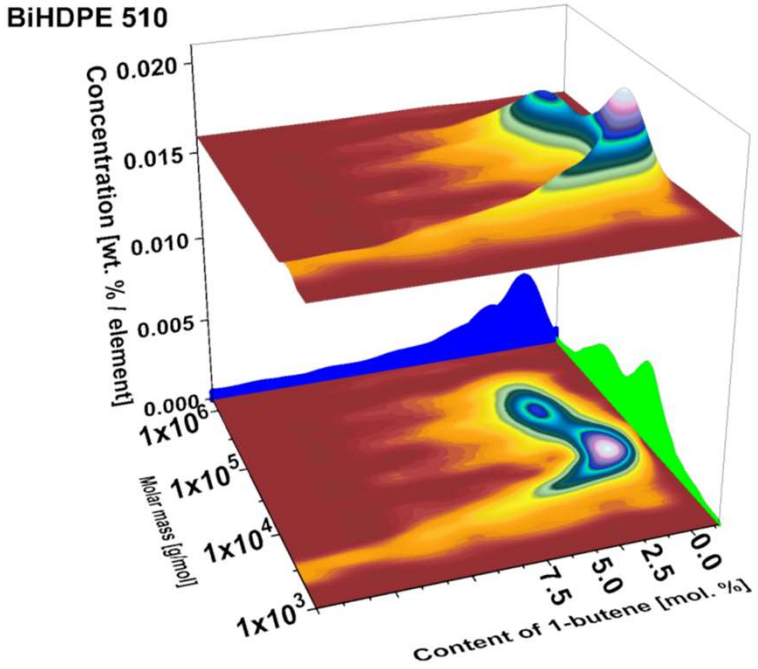
Appl. 3: Multimodal PE



- ELSD: HDPE/LLDPE is 2.5
- IR: HDPE/LLDPE is 1.3



- **HT 2D-LC-IR**
  - Bimodal elution in both dimensions
  - Both HDPE and LLDPE exhibit broad MMD and CCD and they partly overlap
  - LLDPE contains 1-butene from 0 - ~7.5 mol %
  - A long tail of oligomers is evident

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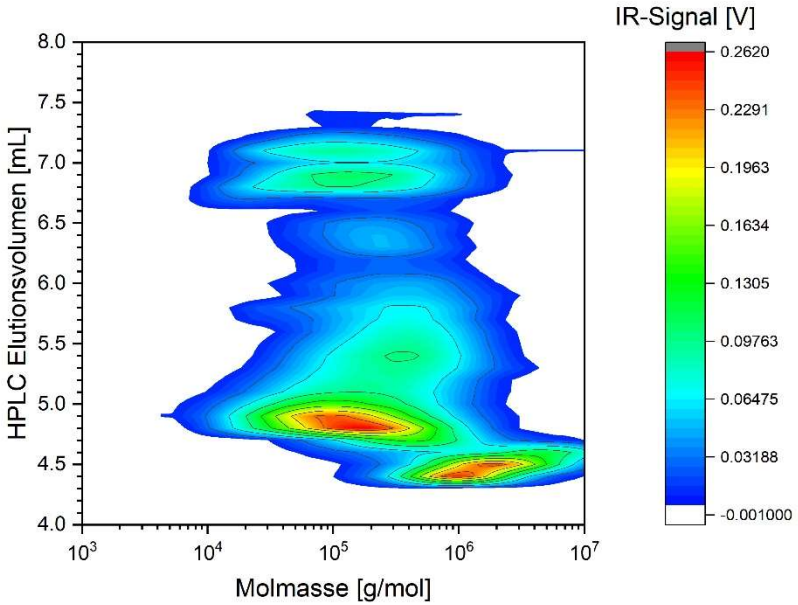
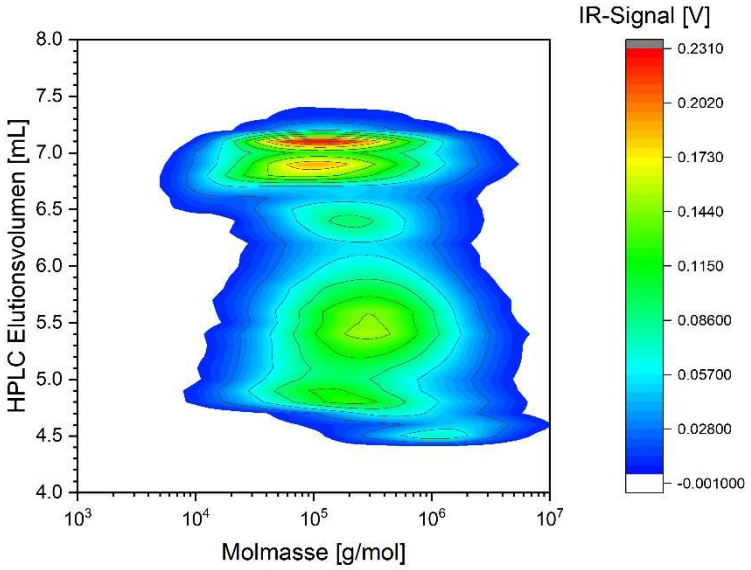
Appl. 4: Tracing and qualifying of recycled material



70 % rec



10 % rec

- Amount of recycled material in a compound can be quantified
- Status of the recycled component can be determined
- Information on short term properties, e.g. mechanics, crack growth, can be predicted

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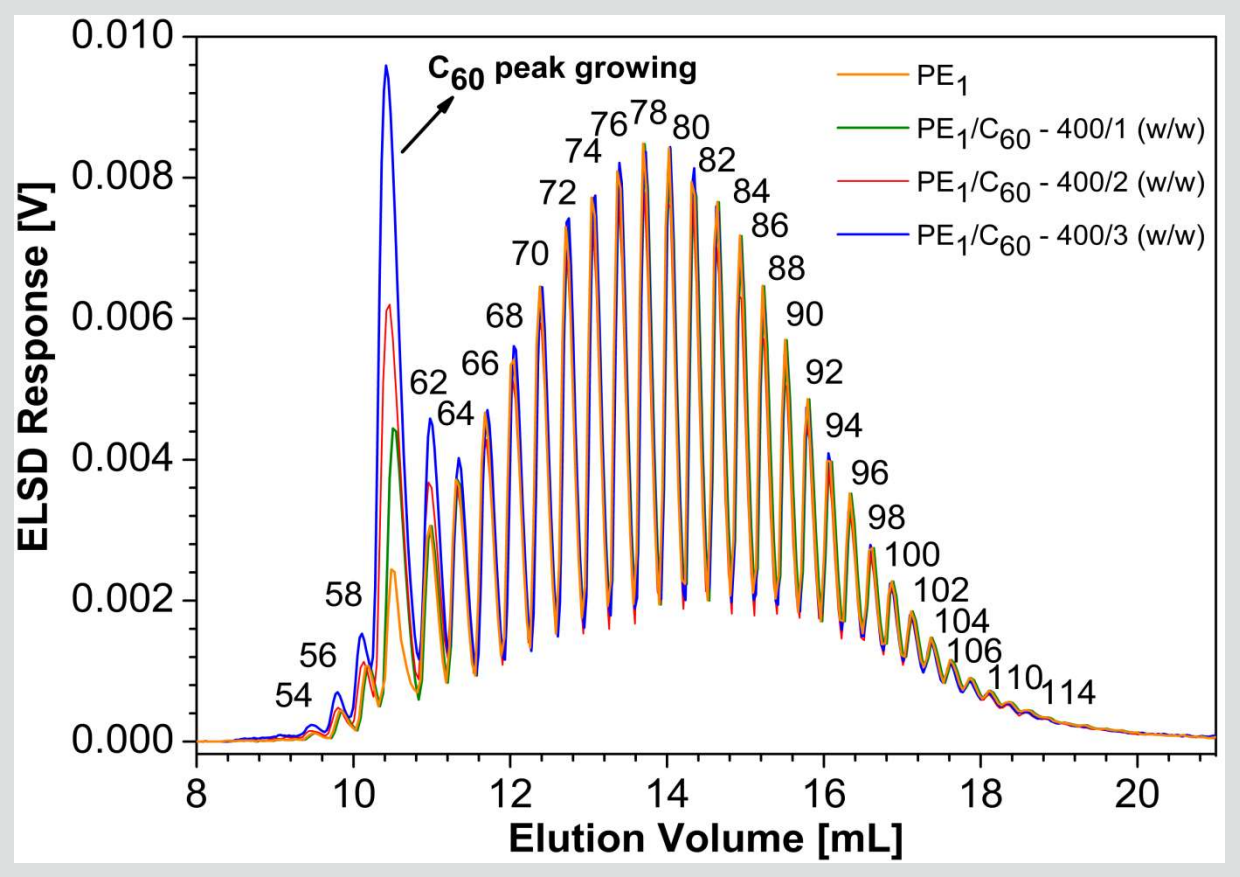
Appl. 5: Oligomer Separation



- Oligomers from C_{54} to C_{114} identified in PE 1 kg/mol. Hypercarb™/Decane→ODCB/ 130 °C

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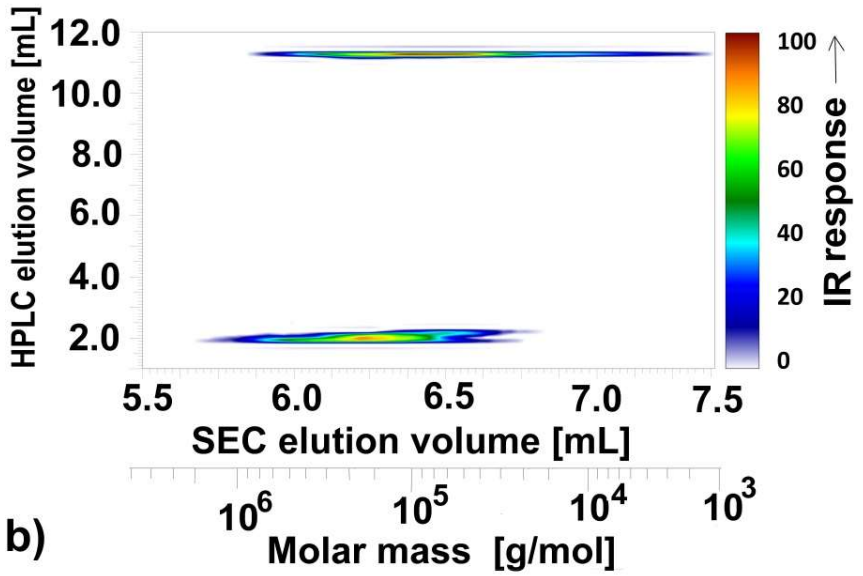
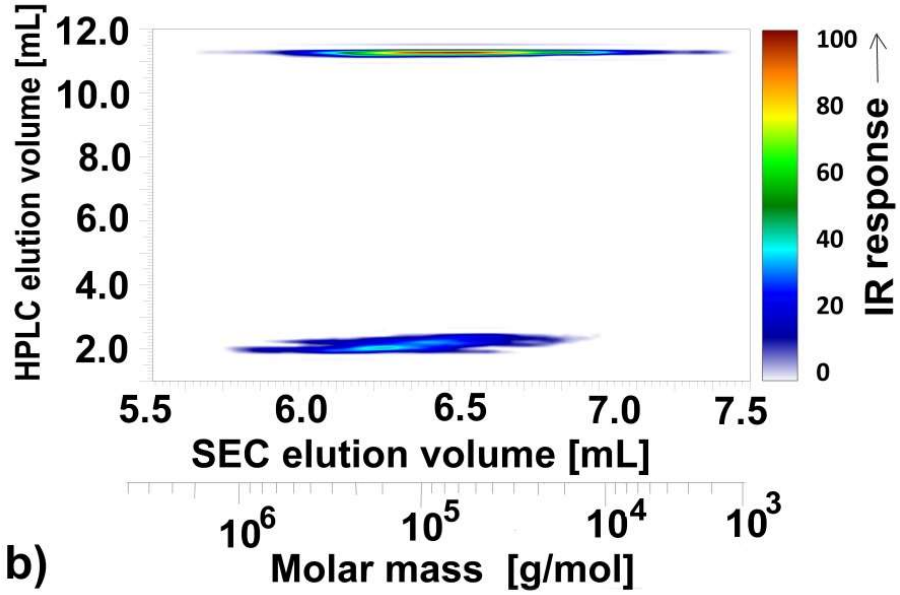
Applic. 6: HT 2D-LC-IR of Grafted Polyolefins

PP-g-MA (1 mol %)



PP-g-MA (1.7 mol %)



- The fraction of grafted material can be quantified
- The molar characteristics of the grafted material can be determined
- PP-g-MA exhibits higher average molar mass compared to iPP

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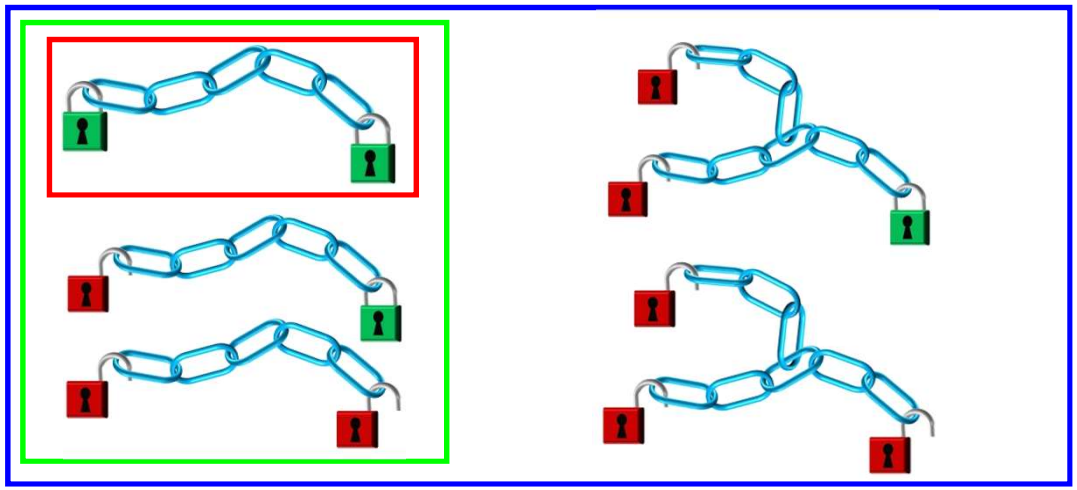
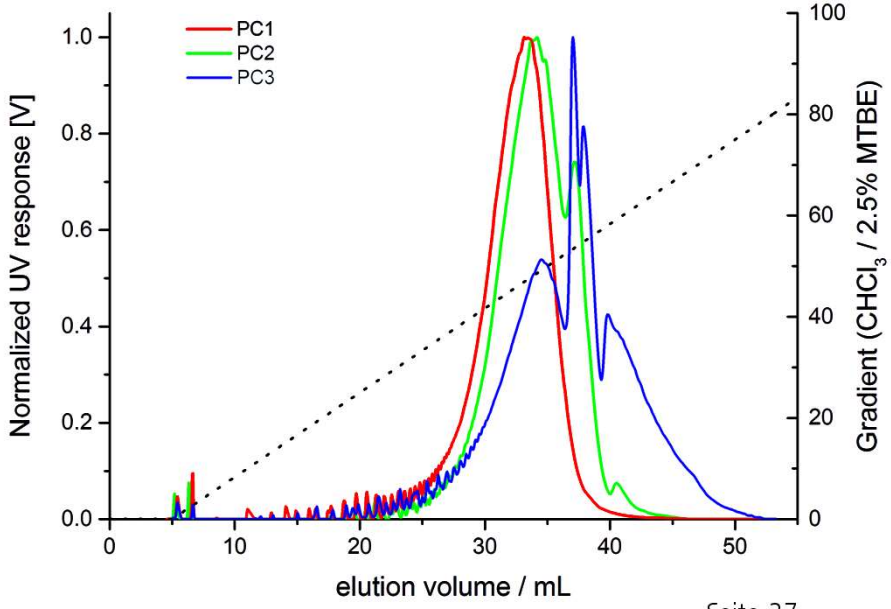
Applic. 5: Solvent gradient at near-critical conditions (SG-NCC)

Poly(bisphenol A carbonate)



- New LC method developed: solvent gradient applied near the critical conditions
- PC1 → **End**-capped + **linear**
- PC2 → **Un**-capped + **linear**
- PC3 → **Un**-capped + **branched**
- Separation according to end-groups and branching indicated



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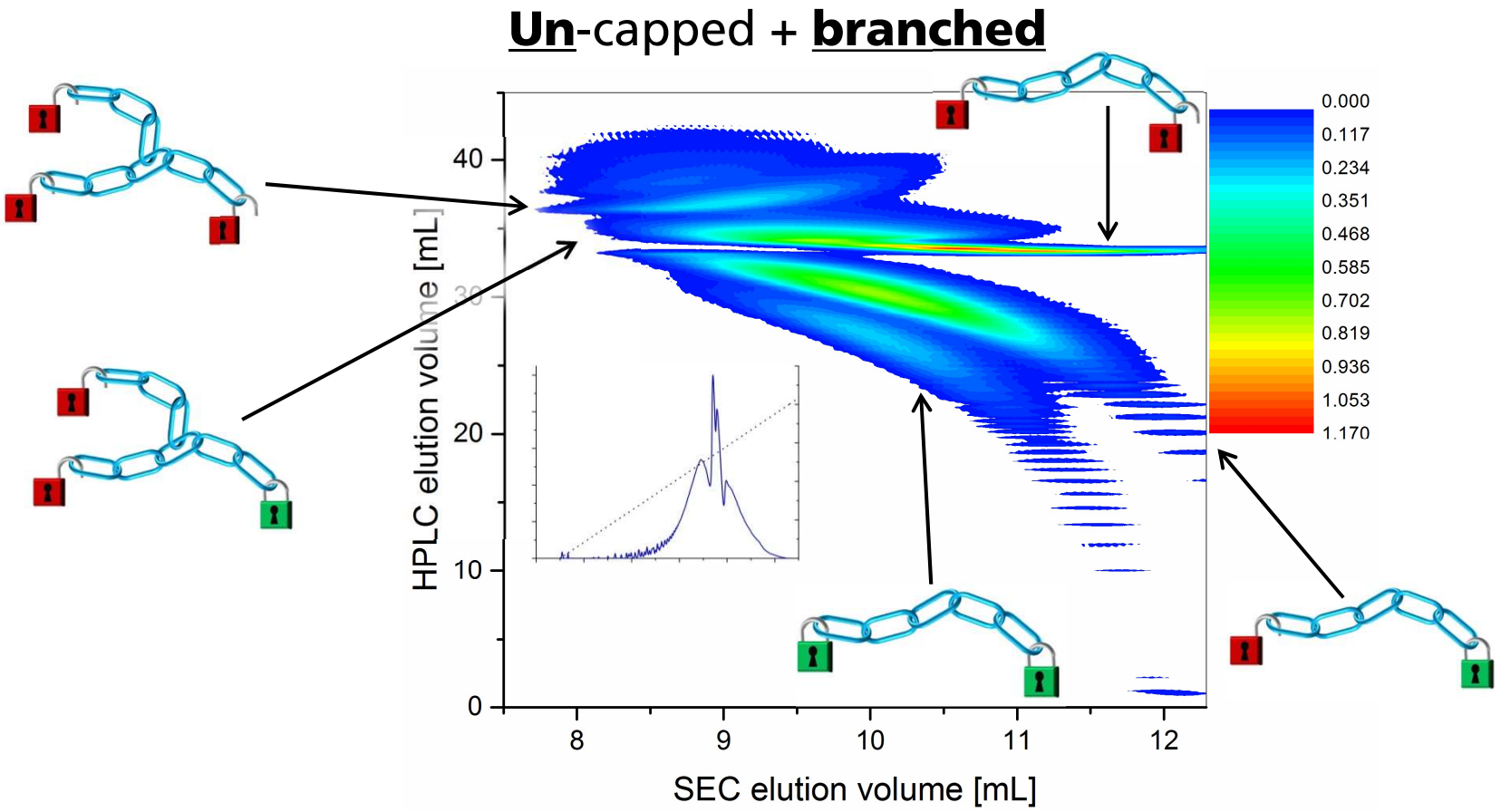
Two-dimensional liquid chromatography (2D-LC)



- Separation according to branches structures

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Additives: Limitations of present analytical attempts

- State of the art: extraction + MS, IR, OIT…..

- Time-consuming

- No comprehensive characterization possible due to diversity of molecular structure for additives

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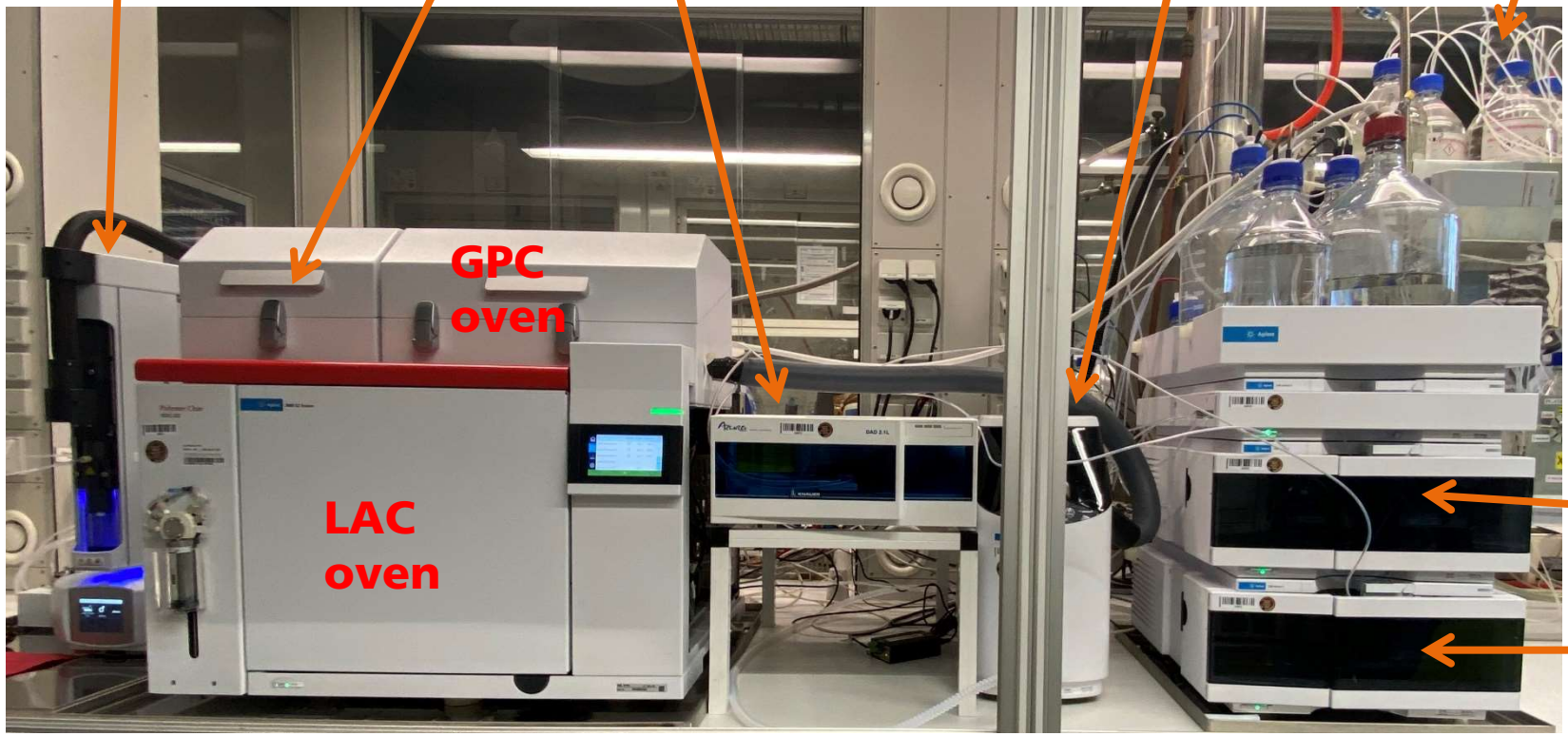
Next Gen High Temperature (HT) 2D-LC



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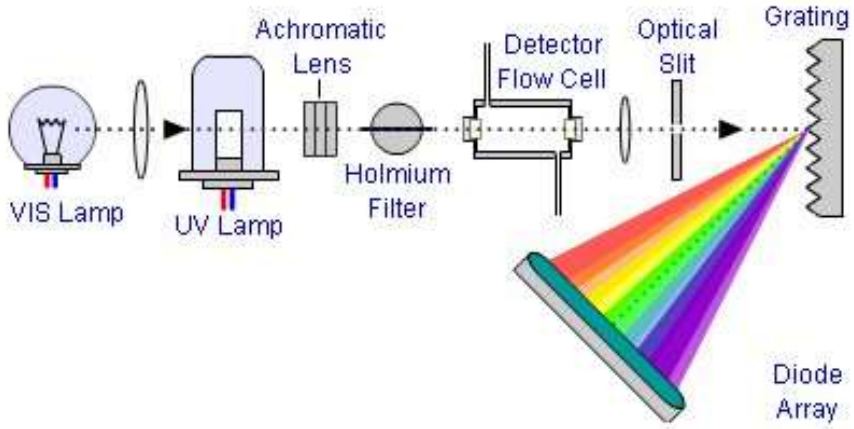
New option: One shot analysis of additives in formulations with HT-GPC-UV



- LC instrumentation with UV detection
- UV-detector, high temperature capable up to 170 °C
- One shot analysis of recyclates with HT-GPC-UV

Big step forward in characterization of polymer formulations!

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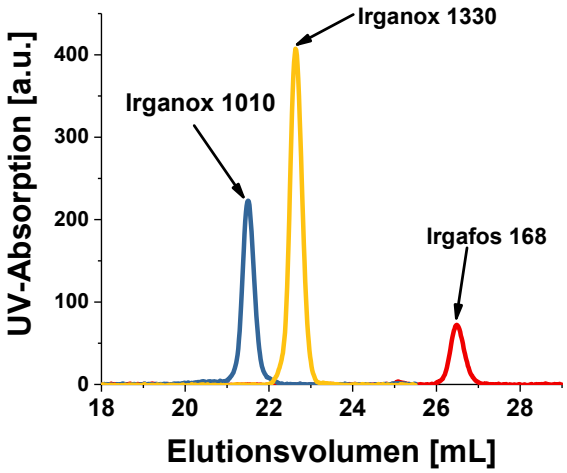
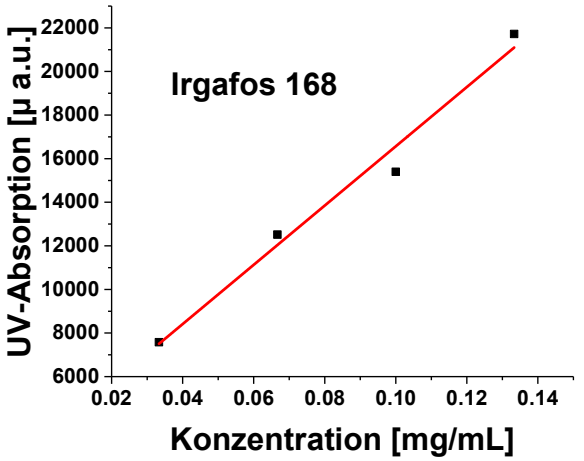
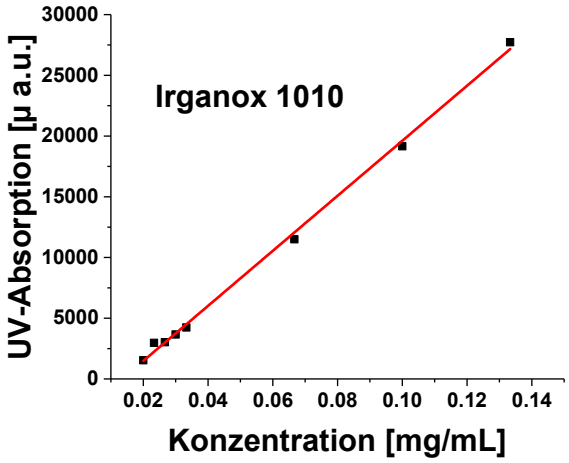
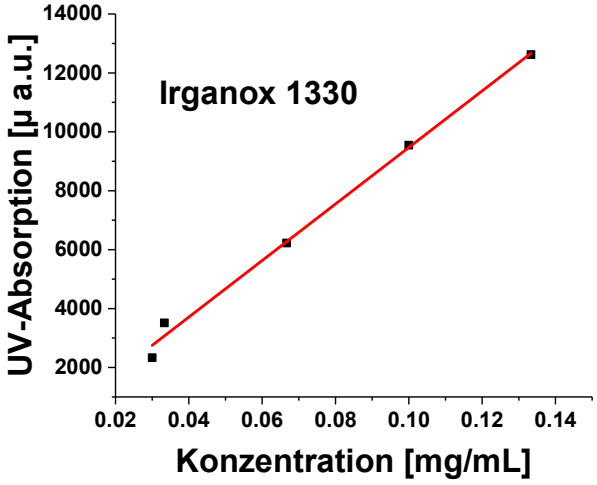
Antioxidantien in HT-GPC-UV









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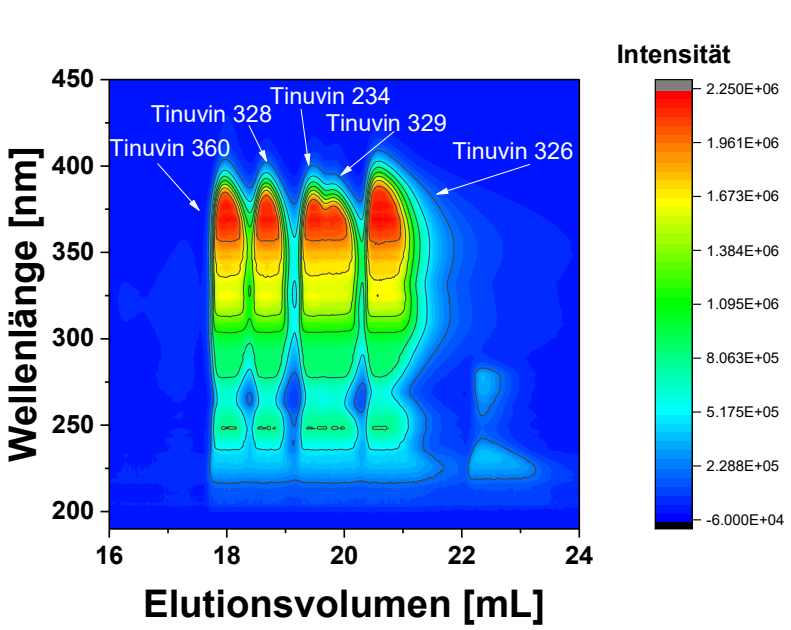
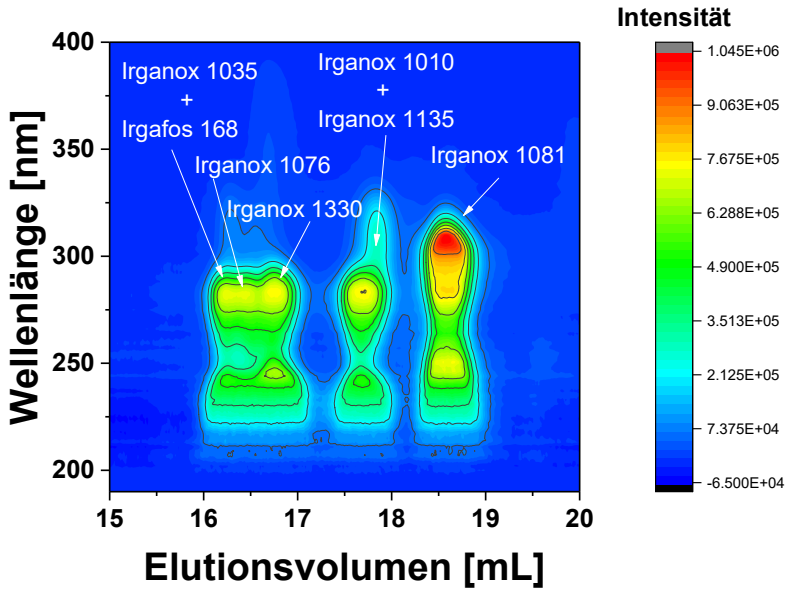
HT-GPC-UV von Additiven
- die typischen Additive in Polyolefinen





- Hochaufgelöste HT-GPC-UV-Trennung von UV-Absorbern und Antioxidantien

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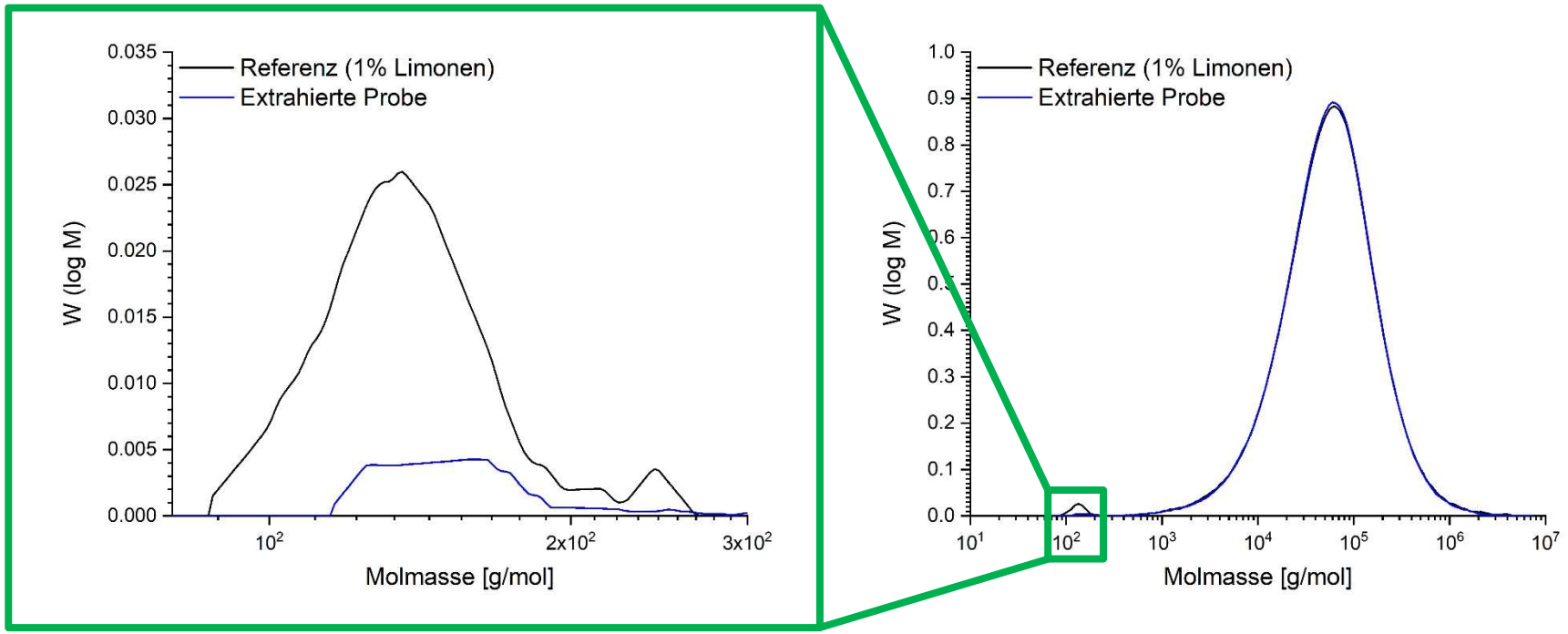
Quantification of Limonen in PE using GPC-IR6



- Limonen = niedermolekular =gut separierbar mittels GPC
- Signifikante Reduktion des Limonengehalts durch Extraktion

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Conclusions

- Olefin copolymers can be separated according to their comonomer content.
- Two-dimensional high temperature liquid chromatography with quantitative detection (HT 2D-LC-IR) enables to fingerprint bivariate distributions (MMD x CCD).
- Polar polyolefins may be suitably derivatized.
- HT GPC-UV allows a rapid one shot analysis of compounds.