Graphit – ungeahnte Perspektiven in der HPLC von Polymeren

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Fraunhofer-Institute for Structural Durability and System Reliability LBF
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The Fraunhofer-Gesellschaft
Main locations in Germany

- 67 institutes
- More than 23,000 employees

The Fraunhofer LBF

Main locations
Other locations
Fraunhofer LBF in Darmstadt

- LOEWE-Center AdRIA
- ZSZ-e
- Main building
- Darmstadt-Kranichstein site
- Darmstadt City site – Division Plastics
- Transfer Center for Adaptronics
Cooperation with Fraunhofer LBF
From fundamental research to marketable products

Services for industry
- Application of proven methods and procedures
- Structural and system analyses
- Consultation
- Qualification of skilled staff

Contract research
- Applied research
- Bilateral R&D cooperation
- Feasibility studies
- ...

Initial research
- Publicly funded projects
- EU, BMWi, BMBF,...

TRL 1
TRL 2
TRL 3
TRL 4
TRL 5
TRL 6
TRL 7
TRL 8
TRL 9

System Test & Operations
System / Subsystem Development
Technology Demonstration
Technology Development
Research to Prove Feasibility
Basic Technology Research
Molecular Characterization

HT HPLC
  - Non-polar/polar
  - Non polar
Challenges in Polymer Analysis

- Multidimensional techniques are required to analyze the chemical heterogeneity
- Classical: fractionations
Liquid Chromatography

- **Potential Benefits**
  - faster than fractionation
  - can be tuned more selective
  - also amorphous samples can be analyzed

- **The Scientific Challenge**
  - Must withstand 160 °C!!!!

Stereo-sequences

Monomer-Sequences

Monomer/Stereo-sequences
Separation Modes

SEC

LAC
LCCC

![Diagram of LCCC](image)

Detector Response [V] vs. Elution Volume [mL]
Screening of Mobile Phases: Solvents for Polyethylene

Polyethylene 260,000 g/mol

2-ethyl-1-hexanol
n-nonylalcohol
cyclohexanone
hexylacetate
cyclohexylacetate
2,2,4,4,6,8,8-heptamethylnonane
n-dodecane/2-ethyl-1-hexanol, 4/5vol.
n-dodecane
decalin/cyclohexanone, 1/3 vol.
decalin/2-ethyl-1-hexanol, 4/5vol.
decalin/cyclohexylacetate, 1/3vol.
1,1,2,2-ethane
decalin/phenylecyclohexane, 1/3vol.
phenylecyclohexane
TCB
decalin
2-chlorotoluene
decalin/methylcyclohexane, 1/3vol.
decalin/cyclohexane, 1/3vol.

Cloud Point Temperature

Temperature (°C), at which precipitation starts

Polyethylene

n
70 80 90 100 110 120 130 140 150 160
Ethylene-Vinylacetate Copolymers High-Temperature Gradient HPLC

Stationary phase: Polygosil 1000; mobile phase: gradient decalin - cyclohexanone (dotted line); temperature: 140 °C; detector: ELSD; sample solvent: decalin (TCB for the PVAc standards)
High-Temperature HPLC Coupled with FTIR for EMA Copolymers

Producer 1

Producer 2

Broad chemical distribution

Narrow chemical distribution

Hyphenation of HPLC and SEC: 2D-LC

The ultimate characterization of a polymer sample, which chromatography may deliver!
HT 2D-LC: Developing the Hardware
Quantitative Detection

Scheme of the instrument
HT 2D-LC-IR of Grafted Polyolefins

PP-g-MA (1 mol %)

- Two spots
- Before the gradient – iPP (elutes in SEC mode)
- In the gradient – iPP-g-MA (symmetric profile)
- PP-g-MA exhibits higher average molar mass compared to iPP
New Stationary Phases
Graphite – Structure Selective Stationary Phase
The Breakthrough

Stationary Phase: Hypercarb™
Mobile Phase: Decanol → TCB

Separation according to composition and microstructure is possible

EP-Copolymers

Random EP copolymers with different average chemical composition

Separation according to ethylene content is possible

EPDM: Influence of Diene

variation in ENB content

Diene adds to retention

R. Chitta, A. Ginzburg, G. van Doremaele, T. Macko, R. Brüll, *Polymer*, 2011, 52(26), 5953 – 5960

Hypercarb™ & 1-decanol→TCB
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

Unique and Identical Segments of Copolymers

Mathematical Operations can be performed on matrices
Improving Signal to Noise in HT 2D-LC

- Multiple injections increase signal intensity
- No shift in spot position
Separation of Oligomers in PE

- Oligomers are present in many polyolefins
- Migrants in food packaging
- Component of Oil
- Analysis by GC-techniques limited
Oligomer Separation – Peak Assignment

- Oligomers from C\textsubscript{54} to C\textsubscript{114} identified in PE 1 kg/mol.
- Hypercarb\textsuperscript{TM}/Decane → ODCB/ 130 °C
TG-NMR of Ethylene/1-Octene

- Concentration decreases at 120 °C (E/O, 37 % Octene)
- Fully reversible, without hysteresis
Portable automatic fraction collector, PAFC, for HT-LC

Software to control the switching valve

Heater

The Core

Side view
Valve and Temperature display

Designed by Tibor

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Preparative GPC of a high molar mass Polyethylene with varying Number of Fractions

3 fractions

5 fractions

8 fractions
Conclusions

- Graphite provides a platform for HPLC of Polyolefins
- Oligomers can be identified in PE
- TG-NMR and Solution DSC prove that the mechanism in TGIC is based on adsorption
- Multiple injections combined with a fraction collector allow preparative isolation of specific components
THE REAL HEROES

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