Mastering Challenges in Polymer Characterization by Chromatography Mass Spectrometry

Till Gründling

Overview

- Polymer Hyphenation Lab at the BASF SE Ludwigshafen Verbundsite

- Mastering Challenges in Polymer Characterization by Chromatography Mass Spectrometry
  - Software tools in polymer LC/MS
  - Method development in Critical Chromatography (LCCC)
Verbund Site Ludwigshafen, Germany

<table>
<thead>
<tr>
<th>Category</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Employees BASF SE</td>
<td>34,769 (as of Dec 31, 2012)</td>
</tr>
<tr>
<td>Site area</td>
<td>10 km²</td>
</tr>
<tr>
<td>Sales products</td>
<td>about 8.5 million metric tons p.a.</td>
</tr>
<tr>
<td>Production facilities</td>
<td>circa 160 production plants</td>
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</tbody>
</table>
In General
- 58 senior scientists/scientists/engineers
- 347 technicians/research associates
- > 300,000 samples/year
- > 6,000 methods
- in 40 laboratories

4 Core Tech Platforms
- Chromatography
- Elemental analysis
- Phys./Chem. analysis
- Spectroscopy

Specialty Laboratories
- Enzyme QC
- Quality control
- ...

Functional Leadership BASF Analytics
Focused on **5 Buildings** at Ludwigshafen Site

- **B009**: NMR-Spectroscopy
- **D216**: Gas- and Trace-Analysis
- **M320**: Elemental Analysis  
  Phys./Chem. Analysis
- **J550**: Formulation Lab  
  Phys./Chem. Analysis
- **E210**: Chromatography  
  Mass Spectrometry  
  Optical Spectroscopy  
  Enzyme Laboratory  
  **Polymer Hyphenation Lab**
Liquid Chromatography

- Molar mass distribution and quantitative composition
- GPC, HPLC, HPLC/IR

Mass Spectrometry

- Structural characterization of large molecules and polymers
- MALDI, LC/MS, GPC/MS
- Py-GC/MS, HT-GC

Bastiaan Staal

Till Gründling
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Polymer Hyphenation Lab
Key Analytical Techniques

- HT-GC
- HPLC/MS, GPC/MS
- MALDI-MS
- Pyrolysis-GC/MS
- HPLC, 2D-LC
- LC/IR
- GPC / SEC
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Chemical Analysis
Across the Entire Molecular Mass Range

Molar Mass Distribution
Chemical Structure
Concentration

Structural Information Content

- MALDI-MS
- GPC/MS
- HPLC/MS
- HPLC
- HT-GC
- Pyrolysis-GC/MS
- GPC/IR
- NMR, IR

Molar Mass

1 kDa 10 kDa 100 kDa 1 MDa
Sample preparation facilities
- Qualitative analysis in complex matrix
- Use of analytical Method-Verbund
- Multi-phase systems
- Formulations, polymer blends, …
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Polymer Hyphenation Lab
Key Analytical Techniques

- HT-GC
- HPLC/MS, GPC/MS
- MALDI-MS
- Pyrolysis-GC/MS
- HPLC, 2D-LC
- LC/IR
- GPC / SEC

Internal – Dr. Till Gründling (GMC/C)
Small molecules are fully described by one mass spectral peak

- Qualitative: Molar mass ($m$)
- Quantitative: Concentration ($c$)
Polymers exhibit chain-length distribution with *n peaks* in the spectrum.

- Qualitative: Molar mass of endgroup ($m_E$) and monomer ($m_{\text{MMA}}$)
- Quantitative: Endgroup concentration ($c_E$) and MWD ($w_n$)

\[ m = m_E + n \cdot m_{\text{MMA}} \]
Co-Polymers exhibit $n \times o$ peaks in the spectrum.

- Qualitative: Molar mass of endgroup ($m_E$) and monomers ($m_{\text{MMA}}$, $m_{\text{Sty}}$)
- Quantitative: Endgroup concentration ($c_E$) and 2D-MMD ($w_{n,o}$)

Theoretical Mass Spectrum

$$m = m_E + n \cdot m_{\text{MMA}} + o \cdot m_{\text{Sty}}$$
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Redundancy – Central Problem of Polymer Mass Spectrometry

- Typical analytical problem:
  - Structure elucidation in formulations
  - Mixture of two polymers of differing functionality

> 100 MS Peaks
5 important values

Mass spectrum: 
- $m/z_{E1,1}, \ldots, m/z_{E1,n}$
- $m/z_{E2,1}, \ldots, m/z_{E2,o}$
- $m/z_{E3,1}, \ldots, m/z_{E3,p}$

Information of interest:
- $m_{MMA}$, $m_{EO}$
- $m_{E2}$, $m_{E3}$, $m_{MAA}$

Theoretical Mass Spectrum

Intensity

$m/z$
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Redundancy – Central Problem of Polymer Mass Spectrometry

- Spectral information can be reduced to a small set of parameters
  - Endgroup mass
  - (Co)monomer mass
  - Chain-length distribution
  - Total concentration

- Spectra are complex due to the chain-length and monomer distributions
  - Bottleneck: Manual spectrum interpretation
Data Processing in SEC/MS and LC/MS

- Handle third dimension added to the data by hyphenation
Direct ESI-MS of a mixture of PEG and functional PMMA

- Dominant distribution of multiply charged PEG
- Weak PMMA distribution (low concentration and lower ion affinity)
Data Processing in SEC/MS and LC/MS

- In-house developed software prototype
- Extraction of polymer distributions from 3D LC/MS data

[Image of software interface with logarithmic plotting]

*logarithmic plotting*

Compare weak and strong distributions across orders of magnitude.
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Data Processing in SEC/MS and LC/MS

- Classical (rectangular) integration of MS data

![Graph showing PEG (z=1), PEG (z=2), and PMMA (z=1) with PMMA barely discernable.]
Adapted 3D (Blob) integration of MS data

Clean PMMA spectrum no PEG overlap
Efficient polymer analysis by HPLC/MS …

… is about processing complex 3D data the right way.
Taking the critical

Out of Critical Chromatography
Polyols are important co-reactants in polyurethane production.

Impurities in polymeric diols hamper performance.

Purity of the base material needs to be ascertained.
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Critical Chromatography (LCCC) by MS

- External manufacturer’s polyol with significant amounts of side products
- Identify $\rightarrow$ MALDI
- Quantify $\rightarrow$ Use Critical Chromatography
Critical Chromatography (LCCC) by MS

- 3 modes of separation in polymer chromatography
- LCCC allows endgroup separation regardless of molecular mass
  - Endgroup-quantification possible with classical detectors

![Diagram showing 3 modes of separation: Size exclusion mode (SEC) with strong eluent, Adsorption chromatography (LAC) with weak eluent, and Critical chromatography (LCCC) with critical composition.](image)
Critical Chromatography (LCCC) by MS

- Preconceptions about LCCC:
  - Method development takes days/weeks
  - Need (to synthesize) molar mass standards of the polymer
  - Maintaining critical conditions is difficult (on bare silica)

- Challenges overcome!
  - Online LC/MS\(^1\) for rapid method development
  - Use analyzed polymer itself as molar mass standard
  - Modern modified silica stationary phases provide robustness

Critical Chromatography (LCCC) by MS

60% DCM

40% n-Hep

m/z

Mono OH
Di OH
Dicarbonate/Cyclics
Critical Chromatography (LCCC) by MS

40% DCM

60% n-Hep
Critical Chromatography (LCCC) by MS

30% DCM

70% n-Hep

Mono OH
Di OH
Dicarbonate/Cyclics

Time (min)

m/z

GPC
Critical Chromatography (LCCC) by MS

20% DCM

80% n-Hep

Mono OH
Di OH
Dicarbonate/Cyclics

GPC near critical
Critical Chromatography (LCCC) by MS

10% DCM

90% n-Hep

Di OH (breakthrough)

Mono OH

Dicarboxylate/Cyclics

m/z
Critical Chromatography (LCCC) by MS

12% DCM

88% n-Hep

DCM

n-Hep

Critical Chromatography (LCCC) by MS

m/z

Mono OH

Di OH

Dicarbonate/Cyclics

LAC

C

N

Time (min)

1 2 3 4 5 6 7 8 9

Mass:

NL: 2.02E7

TIC MS

0848100223kep77_nhep-dcm_88-12_ymc_cn_0,5µl_(1-10verd_dcm)
Critical Chromatography (LCCC) by MS

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14% DCM

86% n-Hep

Time (min)

0 1 2 3 4 5 6 7 8 9

0 50 100

Mono OH

Di OH

Dicarbonate/Cyclics

LAC

m/z

Time (min)

1 2 3 4 5 6 7 8 9

Critical Chromatography (LCCC) by MS
Critical Chromatography (LCCC) by MS

- 16% DCM
- 84% n-Hep

- Mono OH
- Di OH
- Dicarbonate/Cyclics

Time (min): 0, 1, 2, 3, 4, 5, 6, 7, 8, 9

m/z
Critical Chromatography (LCCC) by MS

Mono OH
Di OH
Dicarbonate/Cyclics

Bingo!
Critical Chromatography (LCCC) by MS

30% DCM

70% n-Hep

O H

O H

Mono OH

Di OH

Dicarbonate/Cyclics

Time (min)
Completion of binary scouting run after < 24h
Further „fine tuning“ of high molar mass on LC/ELSD system
Conclusion

- LC/MS is a powerful tool for both:
  - Method development in polymer chromatography
  - In-depth structural characterization of oligomers/polymers

- Polymer mass spectra are complex and information-rich
  - Need dedicated software tools to assist efficient spectrum interpretation
  - Computational data processing algorithms can make MS amenable to a broader set of analytical challenges
Thank You!