Comprehensive Characterization of Natural Rubber Samples using Thermal Field-Flow-Fractionation coupled with MALS and Triple Detection

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• FFF Separation Platform

• Thermal FFF (TF3)

• TF3-MALS and TF3-Triple/Tetra/Penta Detection

• Application Examples
Separation and Detection Platform

Light Scattering Detector PN3621 MALS

Size Separation
- AF2000 Flow FFF
- SC2000 GPC
- CF2000 Centri FFF
- TF2000 Thermal FFF

Intrinsic Viscosity/Branching
- Malvern Zetasizer

Concentration
- UV detector PN3211
- DAD detector PN3241
- Fluori detector PN3411
- ELS detector PN3510
- RI detector PN3150

Viscometer detector PN3310

Particle Size Rg / Molar Mass

Particle Size Rh

Agilent 7900 ICP-MS

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FFF Separation Principle

Separation Mechanism

• Separation in a narrow ribbon-like channel
• Laminar flow inside the channel
• External field perpendicular to the solvent flow
Thermal FFF – Principle

**TF2000: Separation**

\[ V_E \sim DT\Delta T/D \]

**Thermal Diffusion Coefficient**
- Depends on chemical composition

**Applications**
- Rubbers Polymers
- Gels / Latexes
- Cross-linked Polymers

- Thermal gradient up to Δ120°C
- Separation kDa up to several MDa
- Analysis time, 10 – 120min (no upper limit)
- Separation depends on **Size** and **Chemical Composition** ("2 Dimensional"?)
Advantages of Thermal FFF compared to GPC/SEC:

- Excellent separation for high MW extended ‘Exclusion Limit’
- No filtration of gel material, no clogging of columns
- No shear degradation in porous columns / frits
- No interaction with stationary phase
FFF – Triple Detection

- MALS
- Viscometer
- Concentration Detector(s)
Thermal FFF

Setup of TF2000 Thermal FFF with Triple Detection (Penta Detection)
MALS / Viscometer / 3x Concentration Detector

Detector Setup: UV => MALS => Visc => RI => ELSD
Conditions: Solvent = THF, Flow rate = 0.3 mL/min
Alternative Setup: UV => MALS => Split: Visc => Waste and RI => ELSD => Waste
Determination of Mw, Rg, IV and Structure

\[ \text{LS signal} = K_{\text{LS}} \times (dn/dc)^2 \times \text{Conc} \times \text{Mw} \]

\[ \text{RI signal} = K_{\text{RI}} \times (dn/dc) \times \text{Conc} \]

\[ \text{UV signal} = K_{\text{UV}} \times \varepsilon \times \text{Conc} \]

\[ \text{Visco signal} = K_{\text{Visco}} \times [\eta] \times \text{Conc} \]

- \text{MW from MALS + RI}
- \text{Rg from MALS}
- \text{IV from Viscometer + RI}
- \text{Rh from Viscometer + RI + MALS}
- \text{Mark-Houwink plot (log IV vs. log Mw) shows structure and degree of branching}
Results
TFF Applications – PS

Separation of PS standards

System
- TF2000 FFF System
- PN3150 RI Detector

Conditions
- Injection Volume: 20 µL
- Concentration: 2 mg/mL
- Temp. grad. ΔT = 90°K to 0°K
TFF Applications – PS with Pentadetection

DOW PS 1683 / $M_w = 250$ kDa, PD = 2.5

System
- TF2000 FFF System
- PN3621 MALS
- PN3310 Viscometer
- PN3211 UV
- PN3150 RI
- PN3510 ELSD

Conditions
- Injection Volume: 50 µL
- Concentration: 5 mg/mL
- Temp. grad. $\Delta T = 90^\circ K$ to $0^\circ K$
TFFF Applications – PS with Pentadetection

DOW PS 1683 / $M_W = 250$ kDa, PD = 2.5

**System**
- TF2000 FFF System
- PN3621 MALS
- PN3310 Viscometer
- PN3211 UV
- PN3150 RI
- PN3510 ELSD

**Conditions**
- Injection Volume: 50 µL
- Concentration: 5 mg/mL
- Temp. grad. $\Delta T = 90^\circ K$ to $0^\circ K$
TF3 enables separation of molecules with the same hydrodynamic volume according to their chemical composition!
TFF Applications – SBR Rubber with Pentadetection

- MALS
- Viscometer
- RI
- ELSD
- UV
Application Example: Natural Rubber
TFFF Applications - Natural Rubber

• Nanoscale impurities with same size separated according to different chemical composition
TFFF Applications – Natural Rubber with Pentadetection

Natural Rubber Sample (Polyisoprene)

System
- TF2000 FFF System
- PN3621 MALS
- PN3310 Viscometer
- PN3211 UV
- PN3150 RI
- PN3510 ELSD

Conditions
- Injection Volume: 50 µL
- Concentration: 5 mg/mL
- Temp. grad. \( \Delta T = 90^\circ K \) to 0\(^\circ K\)

Stiff chain structure in low MW area

\( a = 0.98 \)
System
- TF2000 FFF System
- PN3621 MALS
- PN3310 Viscometer
- PN3211 UV
- PN3150 RI
- PN3510 ELSD

Conditions
- Injection Volume: 50 µL
- Concentration: 5 mg/mL
- Temp. grad. $\Delta T = 90^\circ$K to 0$^\circ$K

Natural Rubber Sample

More compact structure in high MW area (branching?)

$$a = 0.49$$

$$a = 0.98$$
The fractogram shows a system start peak at 11 min.
The 1st peak – the main peak – was detected between 15 - 50 min by light scattering and ELSD detection.
A 2nd peak was detected at 54 min predominantly by light scattering.
Overlay: Molar Mass and LS Signal

- The molar mass was calculated from MALS and ELSD data
- Literature value for $dn/dc = 0.124$ mL/g
- In the 1st peak the sample contains rubber material with a molar mass of appr. $4.7 \times 10^5$ g/mol (w-average) and in the 2nd peak of $3.6 \times 10^8$ g/mol.

Conditions

- Molar Mass (red dots)
- LS Signal (blue trace)
- Fitting by Random Coil Model

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$M_w$ [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Peak</td>
<td></td>
</tr>
<tr>
<td>13.0 – 48.5 min</td>
<td>$n$-Average</td>
</tr>
<tr>
<td></td>
<td>$w$-Average</td>
</tr>
<tr>
<td></td>
<td>$z$-Average</td>
</tr>
<tr>
<td>2. Peak</td>
<td></td>
</tr>
<tr>
<td>48.5 – 56.0 min</td>
<td>$n$-Average</td>
</tr>
<tr>
<td></td>
<td>$w$-Average</td>
</tr>
<tr>
<td></td>
<td>$z$-Average</td>
</tr>
</tbody>
</table>
Overlay: Radius of Gyration and LS Signal

- The Radius of Gyration was calculated from MALS angular data.
- The main/1\textsuperscript{st} peak shows a Radius of Gyration of 42 nm (z-average) and the 2\textsuperscript{nd} peak a Radius of Gyration of 218 nm.

### Conditions

- Radius of Gyration (red dots)
- LS Signal (blue trace)
- Fitting by Random Coil Model

<table>
<thead>
<tr>
<th>Peak</th>
<th>Time [min]</th>
<th>n-Average</th>
<th>w-Average</th>
<th>z-Average</th>
</tr>
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<tr>
<td>1. Peak</td>
<td>13.0 – 48.5</td>
<td>23</td>
<td>31</td>
<td>42</td>
</tr>
<tr>
<td>2. Peak</td>
<td>48.5 – 56.0</td>
<td>65</td>
<td>107</td>
<td>218</td>
</tr>
</tbody>
</table>
The sample shows a multimodal distribution. For the 1\textsuperscript{st} fraction (13 – 48.5 min) the distribution is in the range of $9.2 \times 10^4 – 2.8 \times 10^6$ g/mol and for the 2\textsuperscript{nd} fraction (48.5 – 56 min) in the range of $2.7 \times 10^6 – 2.3 \times 10^9$ g/mol. The sample contains 1.3 % of high molar mass material (gel). Calculation based on concentration detector signal.
TFFF Applications - Natural Rubber

Fractal Dimension

System
- PN5300 Auto Injector
- AF2000 FFF System
- PN3621 MALS Detector
- PN3150 RI Detector
- PN3510 ELSD

Conditions
- Injection Volume: 20 µL
- Concentration: 2 mg/mL
The Fractal Dimension was evaluated for 2 different regions. For the 1st region of the fractogram (17.5 – 44.6 min) the Fractal Dimension is 1.78 and for the 2nd region (51.6 – 54.8 min) 2.92. The Fractal Dimension change indicates that in the 2nd part of the fractogram there is material with a higher density, indicating cross linking or branches.
Summary

Thermal FFF is a Powerful Method for Polymer and Biopolymer Characterization

• Increased resolution for high molar mass species
• Huge flexibility in choice of fractionation power (gradient)
• No interaction with stationary phase / no artifacts
• No degradation due to shear stress during the separation
• No filtration by stationary phase or frits
• Separation according to molecular weight and size as well as according to chemical composition offers new horizons for further applications
Thank you for your Attention