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

Dr. Gerhard Heinzmann, Postnova Analytics GmbH, Germany

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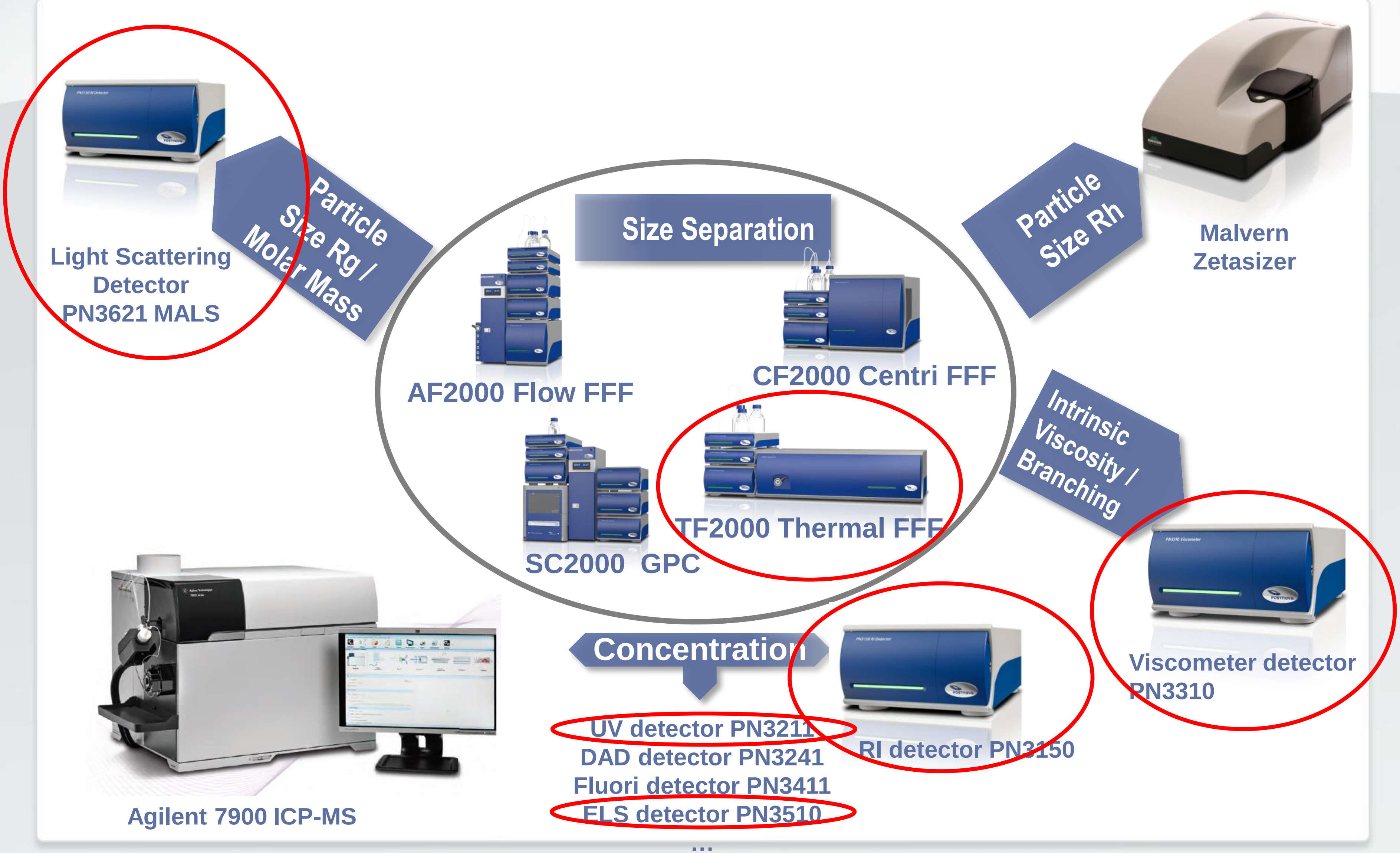
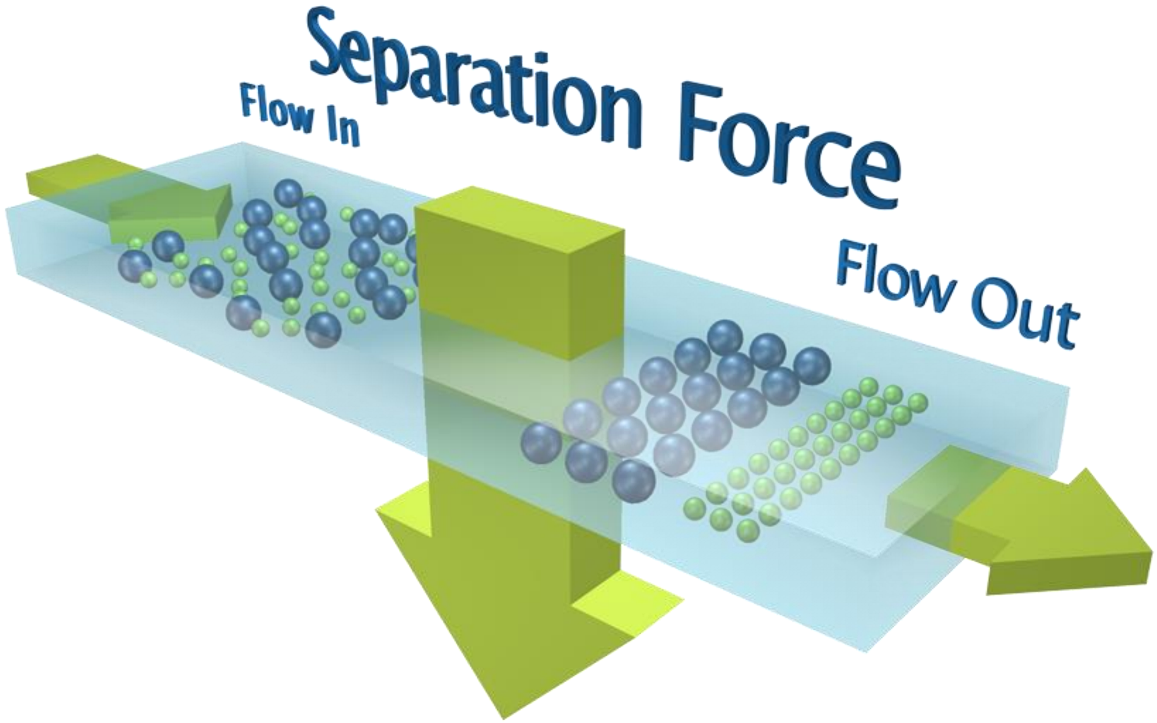
- FFF Separation Platform
- Thermal FFF (TF3)
- TF3-MALS and TF3-Triple/Tetra/Penta Detection
- Application Examples

Separation and Detection Platform



FFF Separation Principle

Separation Mechanism



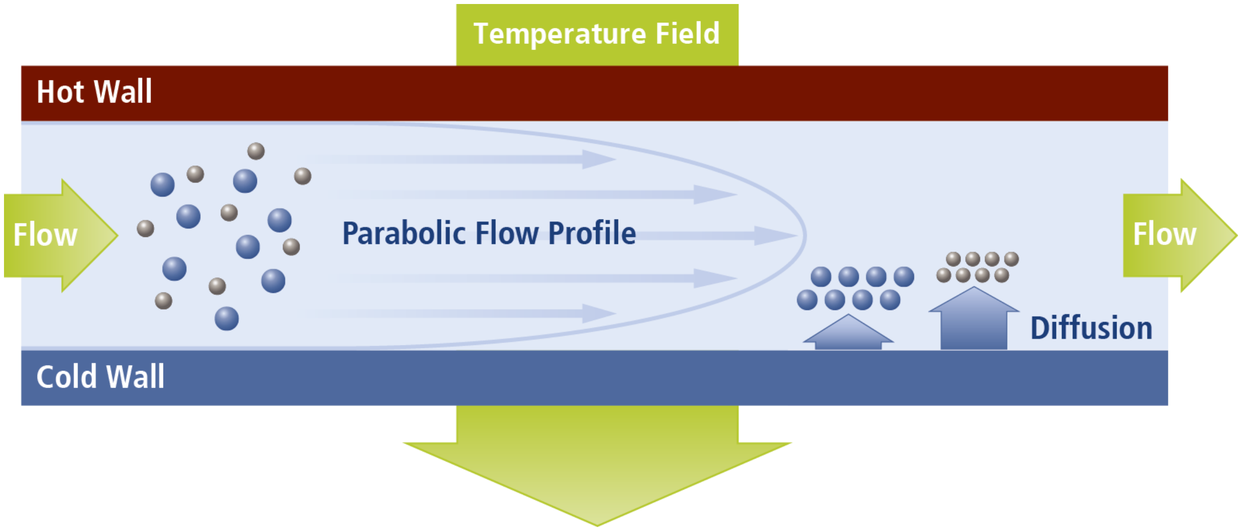
- Separation in a narrow ribbon-like channel
- Laminar flow inside the channel
- External field perpendicular to the solvent flow

Thermal FFF – Principle

TF2000: Separation

Thermal Diffusion Coeffcient
-> Depends on chemical composition

$V_E \sim D_T \Delta T / D$



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”?)

Thermal FFF vs. GPC/SEC

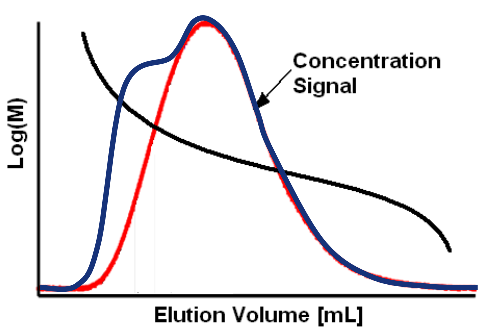
Advantages of Thermal FFF compared to GPC/SEC:

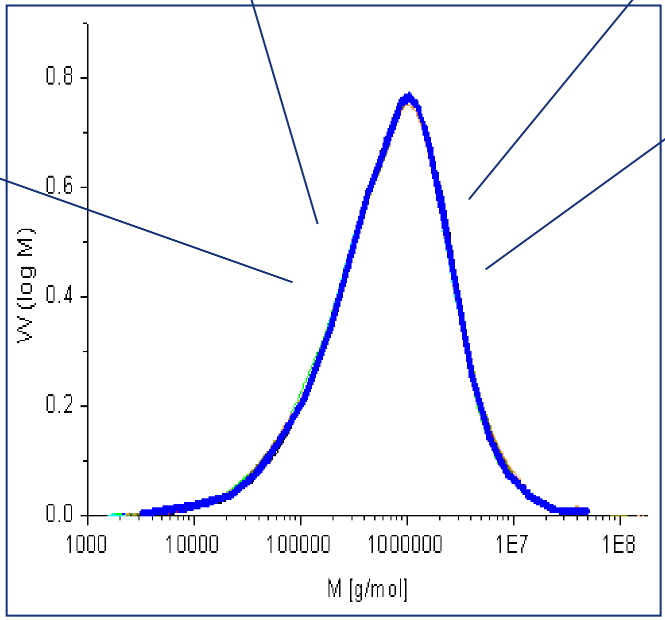
No shear degradation in porous columns / frits

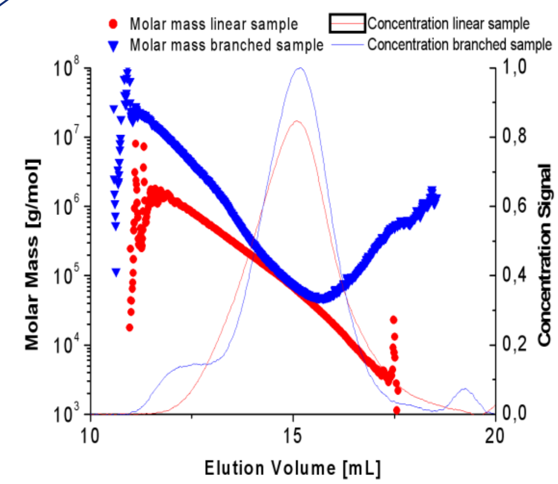
No filtration of gel material, no clogging of columns

No interaction with stationary phase

Excellent separation for high MW ➡ extended ´Exclusion Limit´







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

$$LS_{signal} = K_{LS} * (dn/dc)^2 * Conc * Mw$$

$$RI_{signal} = K_{RI} * (dn/dc) * Conc$$

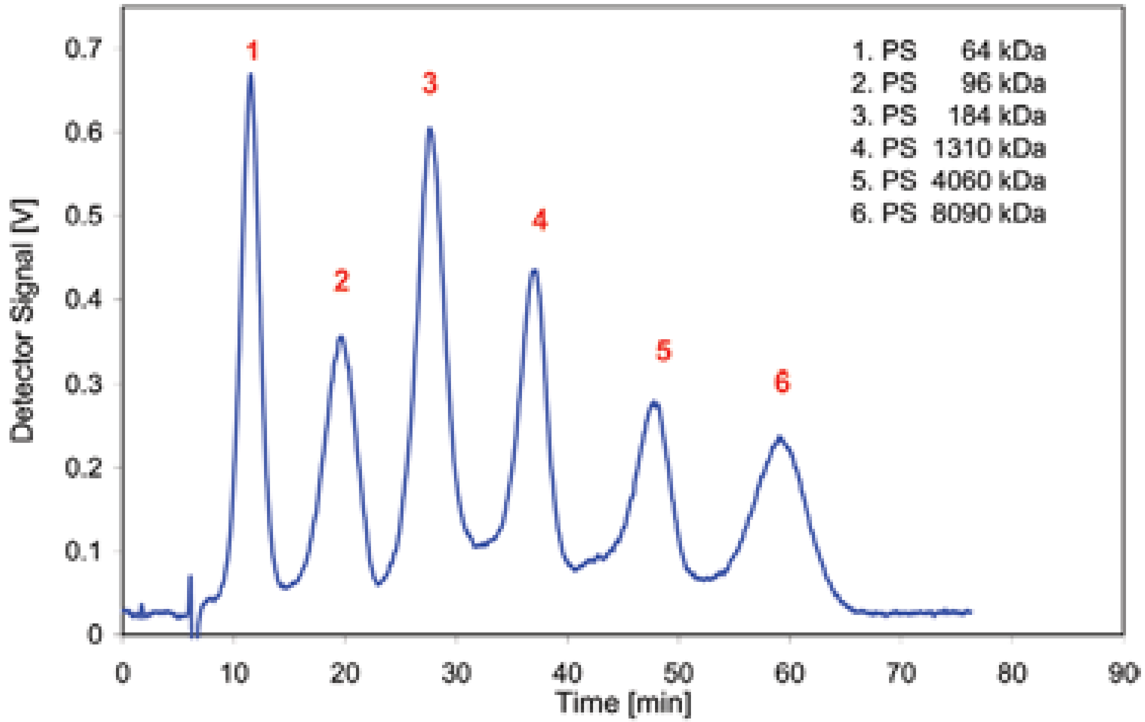
$$UV_{signal} = K_{UV} * \varepsilon * Conc$$

$$Visco_{signal} = K_{Visco} * [\eta] * Conc$$

- **MW from MALS + RI**
- **Rg from MALS**
- **IV from Viscometer + RI**
- **Rh from Viscometer + RI + MALS**
- **Mark-Houwink plot (log IV vs. log Mw) shows structure and degree of branching**

Results

Separation of PS standards



System

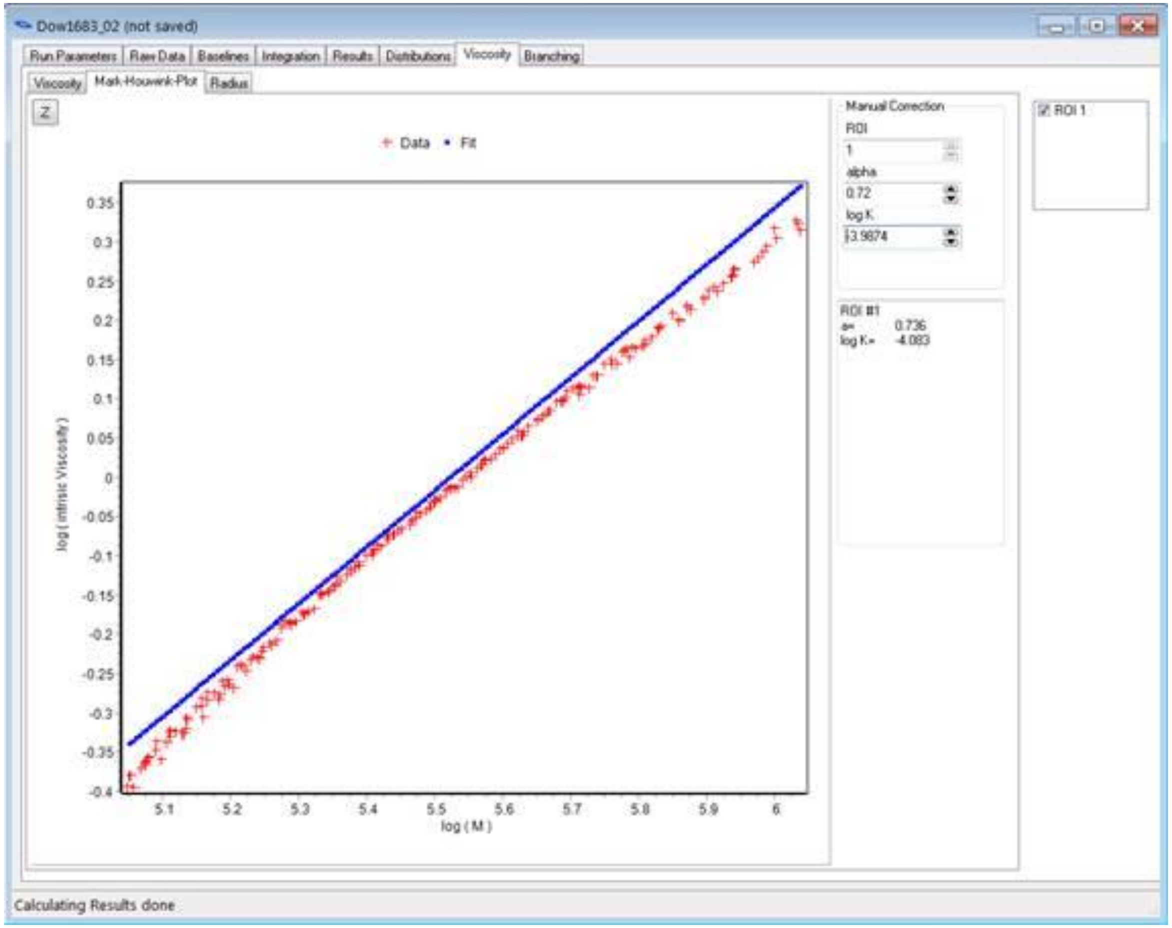
- TF2000 FFF System
- PN3150 RI Detector

Conditions

- Injection Volume: 20 µL
- Concentration: 2 mg/mL
- Temp. grad. ΔT = 90°K to 0°K

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. ∆T = 90°K to 0°K

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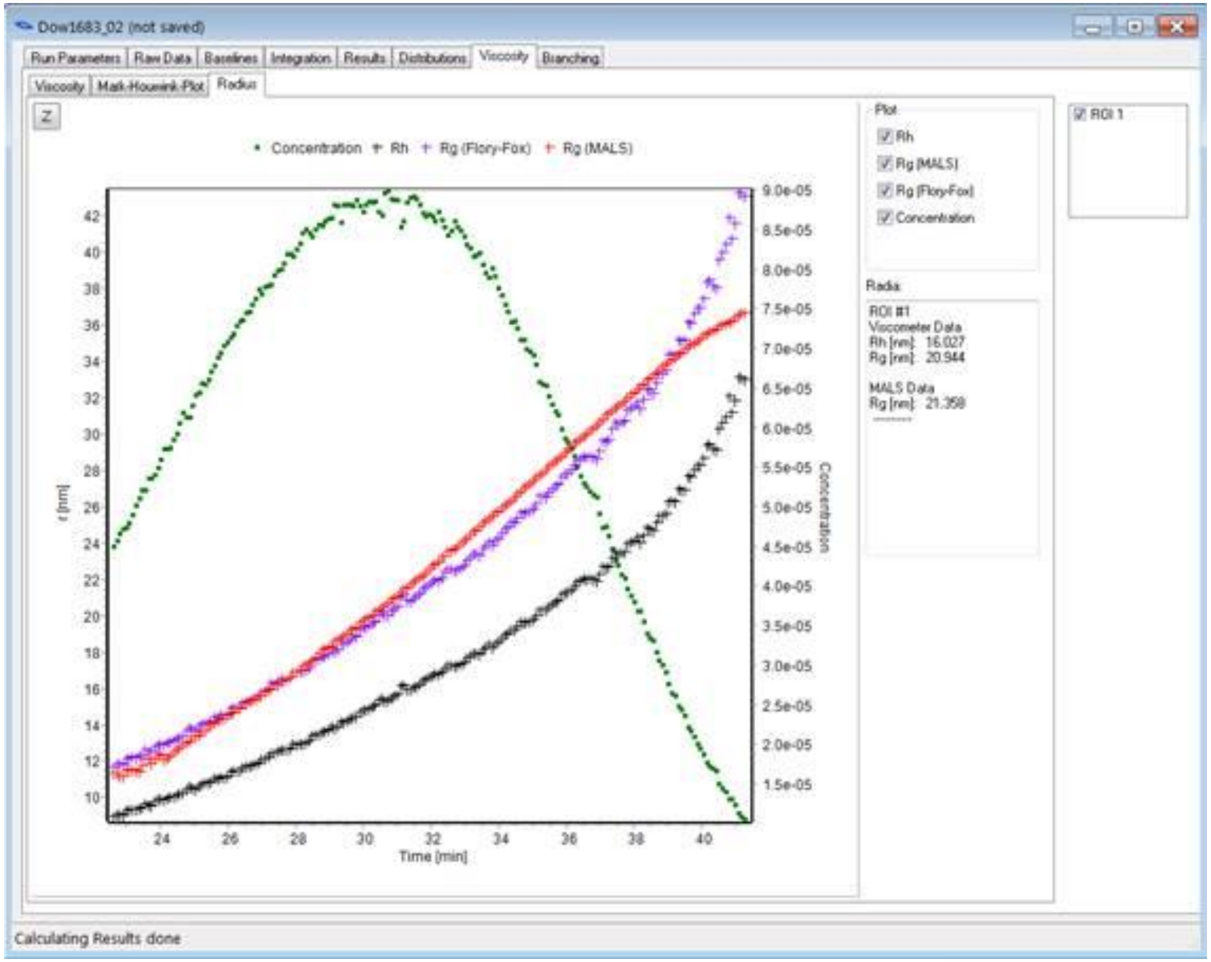

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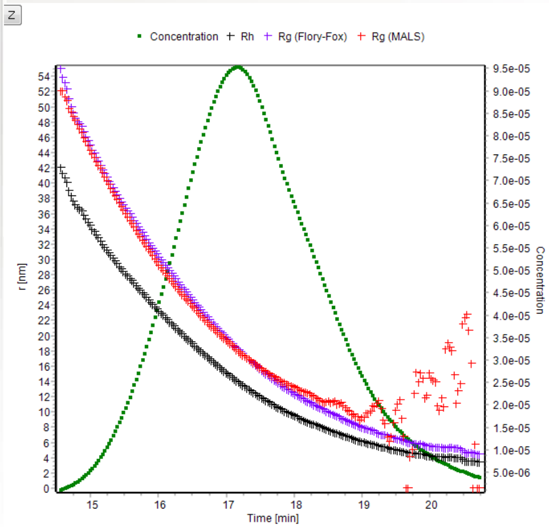
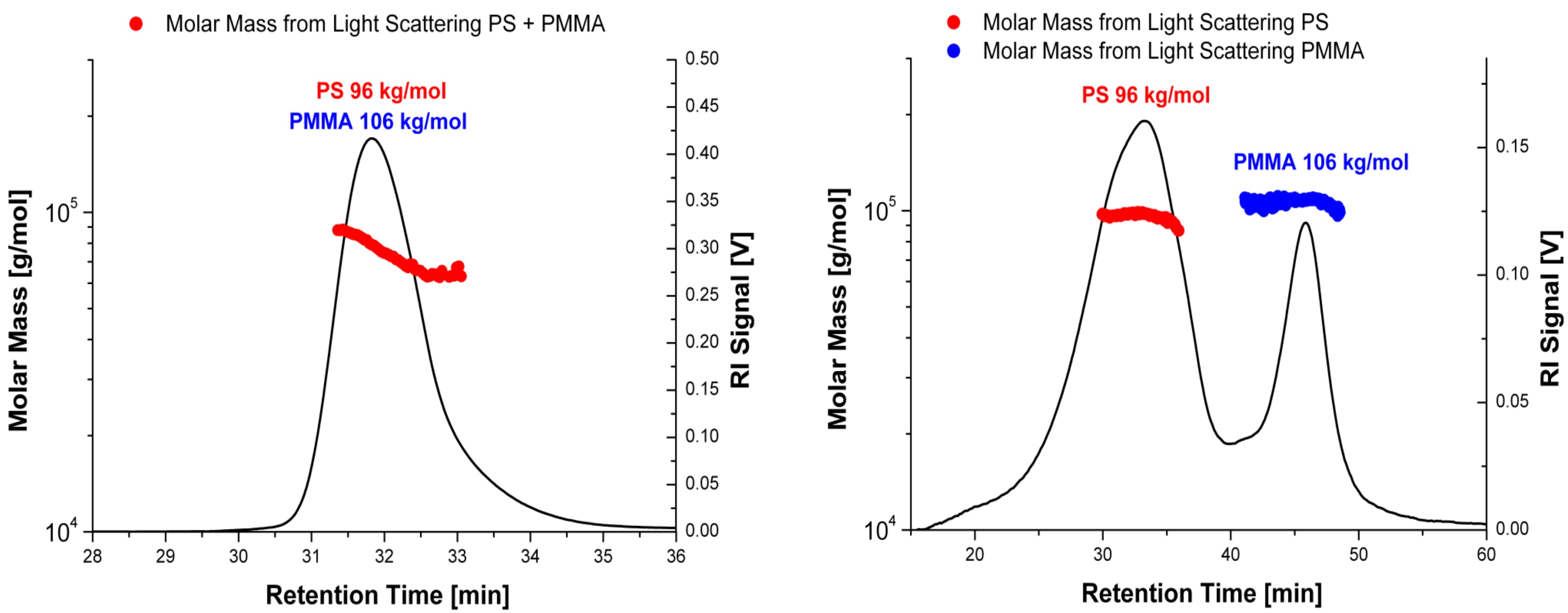


TFFF - Separation by Chemical Composition

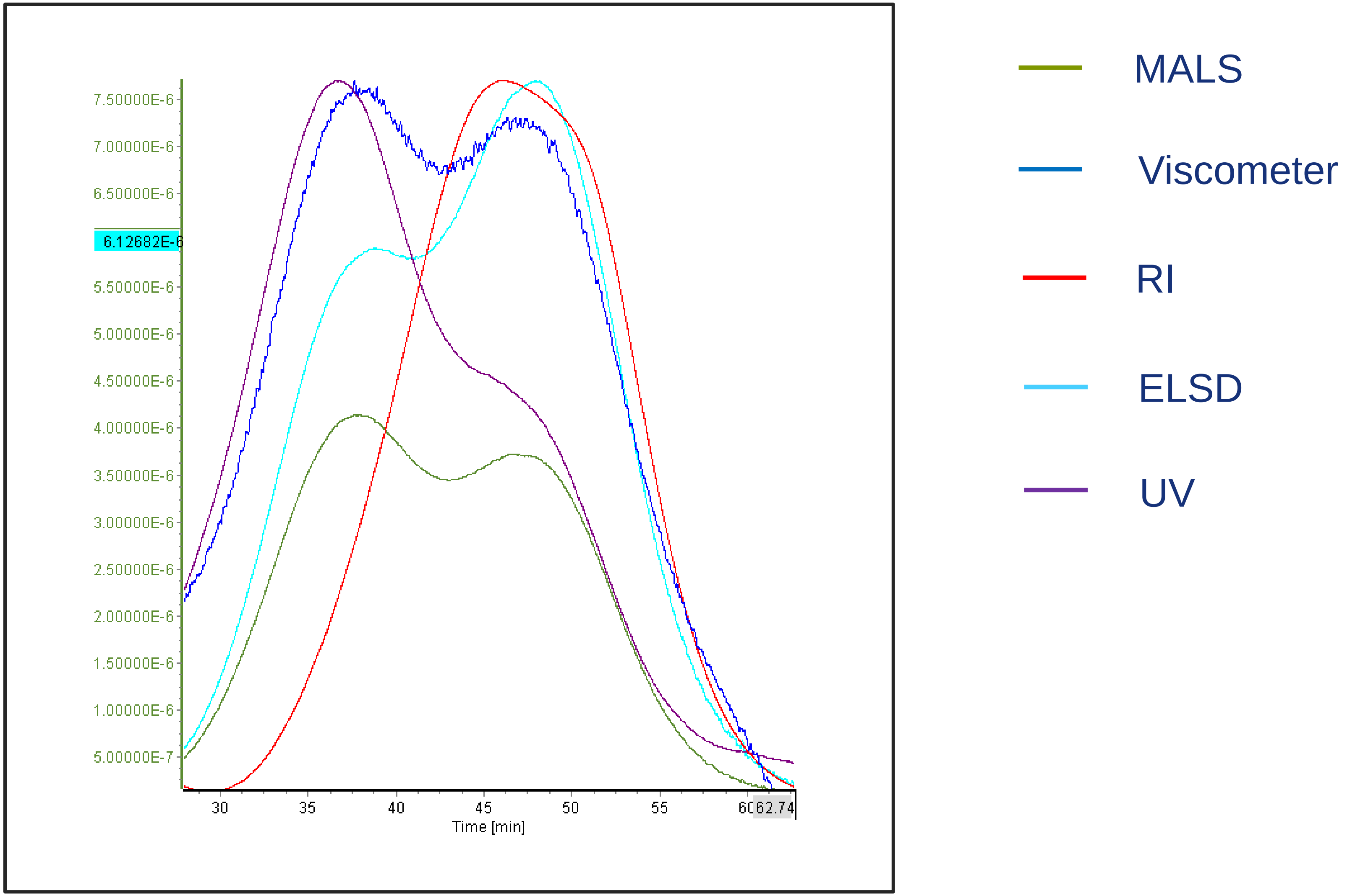
Separation of PS and PMMA-Standards with same R_h

SEC vs. Thermal FFF (TF3)



TF3 enables separation of molecules with the same hydrodynamic volume according to their chemical composition!

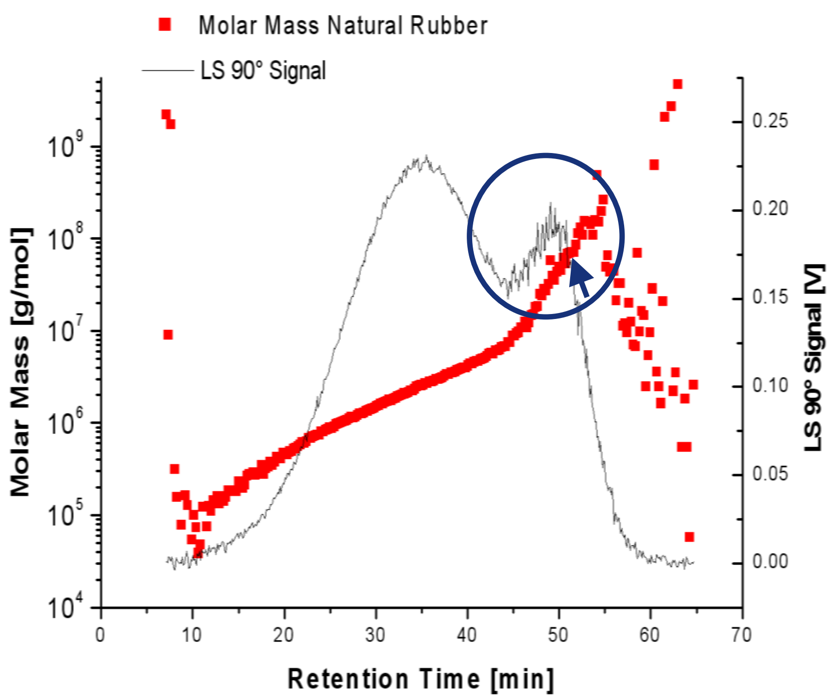
TFFF Applications – SBR Rubber with Pentadetection



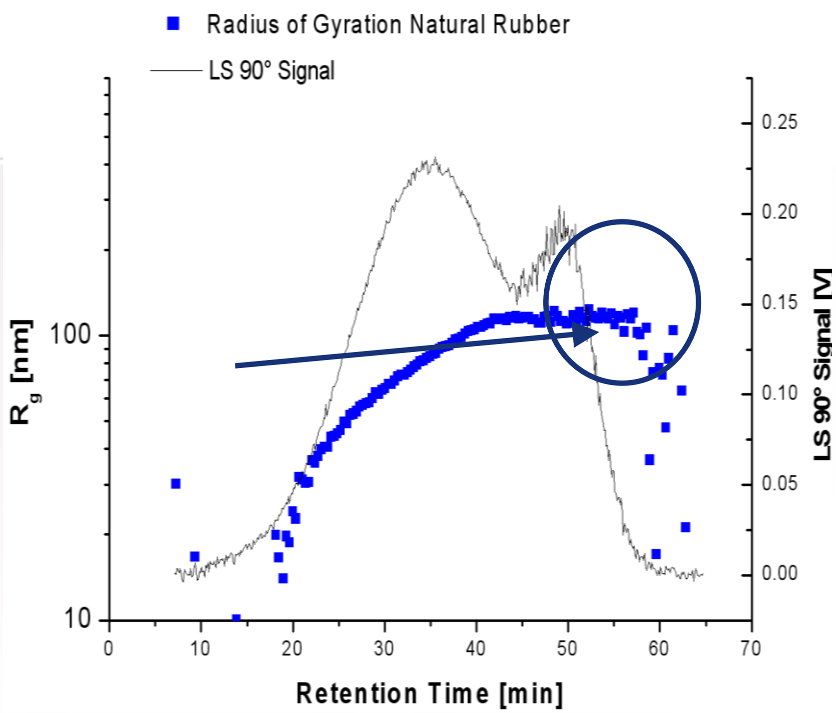
Application Example: Natural Rubber

TFFF Applications - Natural Rubber

Molar Mass



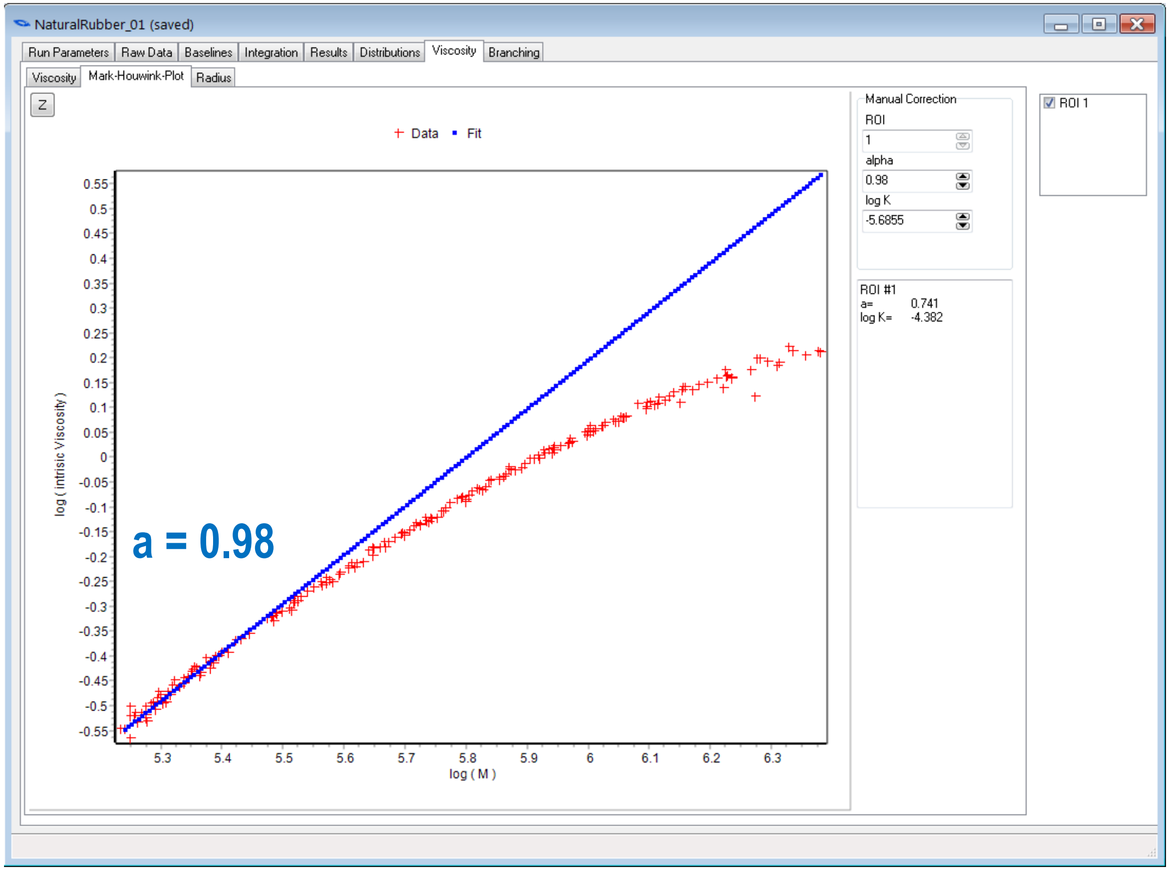
Radius of Gyration



- ***Nanoscale impurities with same size separated according to different chemical composition***

TFFF Applications – Natural Rubber with Pentadetection

Natural Rubber Sample (Polyisoprene)



Stiff chain structure in low MW area

System

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- PN3621 MALS
- PN3310 Viscometer
- PN3211 UV
- PN3150 RI
- PN3510 ELSD

Conditions

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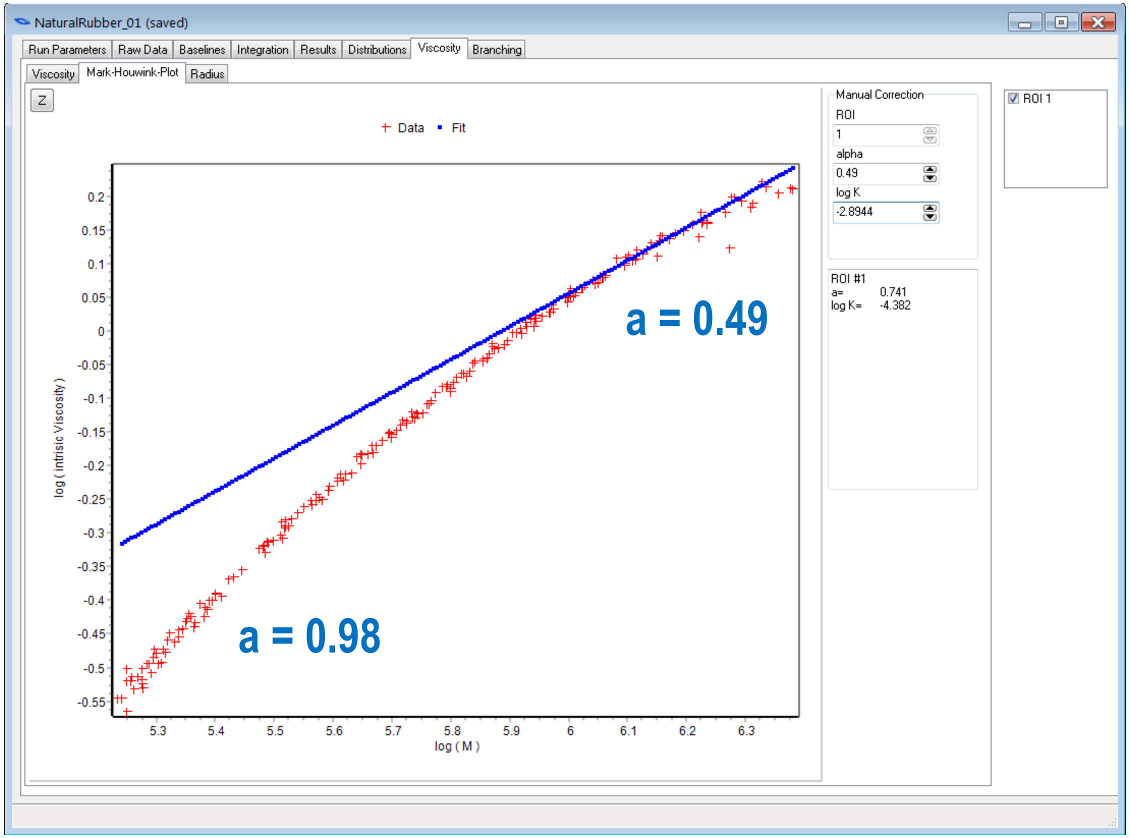
- Concentration: 5 mg/mL
- Temp. grad. ΔT = 90°K to 0°K

TFFF Applications – Natural Rubber with Pentadetection

Natural Rubber Sample



System

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

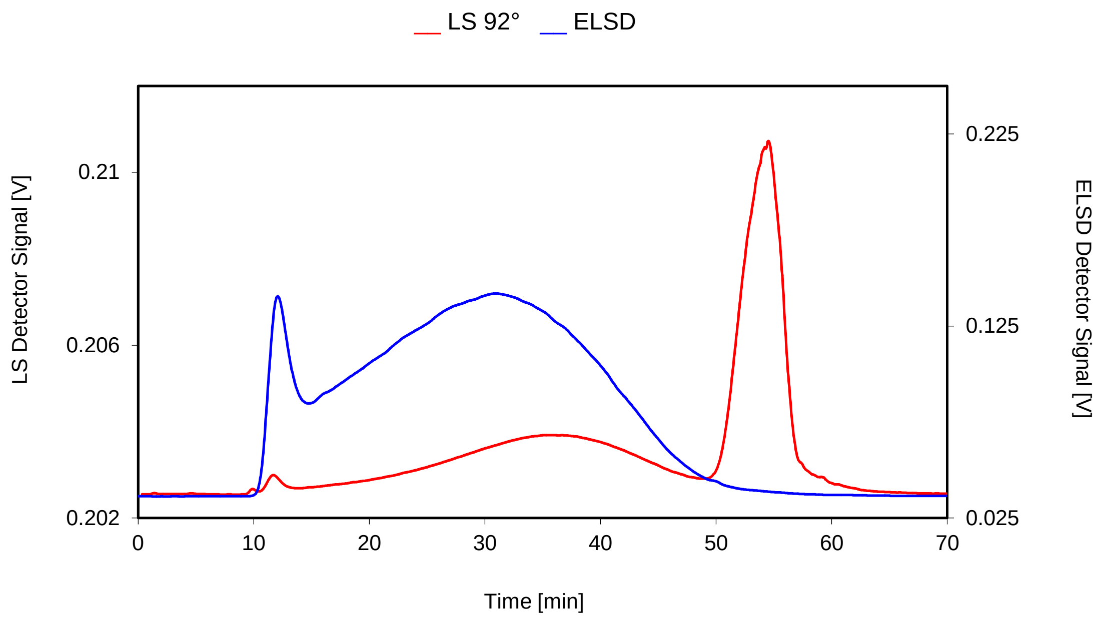
Conditions

- Injection Volume: 50 µL
- Concentration: 5 mg/mL
- Temp. grad. ΔT = 90°K to 0°K

More compact structure in high MW area (branching?)

TFFF Applications - Natural Rubber

Raw Data Fractogram of TF3 - MALS and ELSD



- 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.

System

- PN5300 Auto Injector
- TF2000 Thermal FFF
- ELSD
- PN3621 MALS (92° SLS)

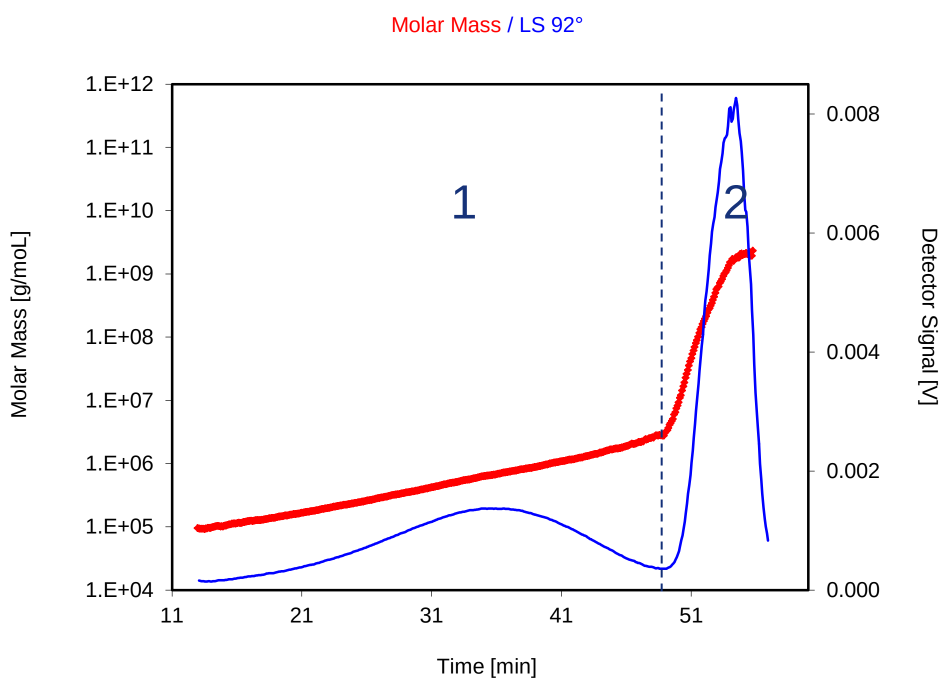
Conditions

- Injection Volume: 100 µL
- Concentration: 2.0 mg/mL
- LS 92°(red trace)
- ELSD (blue trace)

POSTNOVA

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 x 10^5 g/mol (w-average) and in the 2nd peak of 3.6 x 10^8 g/mol.



Conditions

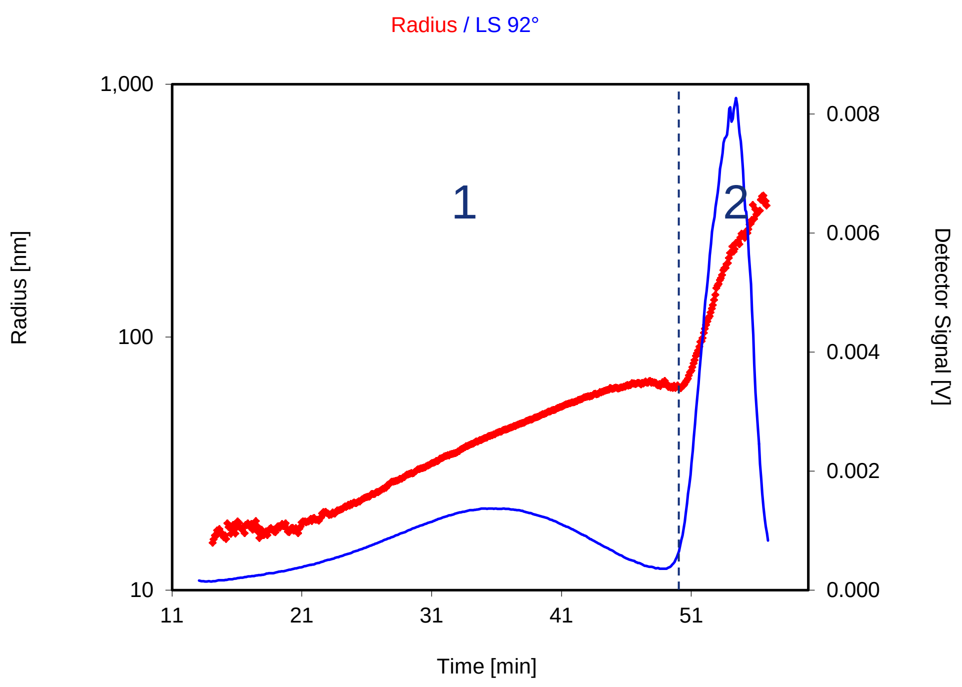
- Molar Mass (red dots)
- LS Signal (blue trace)
- Fitting by Random Coil Model

		M_w[g/mol]
1. Peak 13.0 – 48.5 min	*n*-Average	2.7 x 10^5
	***w*-Average**	**4.7 x 10^5**
	z-Average	8.1 x 10^5
2. Peak 48.5 – 56.0 min	*n*-Average	8.1 x 10^6
	***w*-Average**	**3.6 x 10^8**
	z-Average	1.5 x 10^9

TFFF Applications - Natural Rubber

Overlay: Radius of Gyration and LS Signal

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



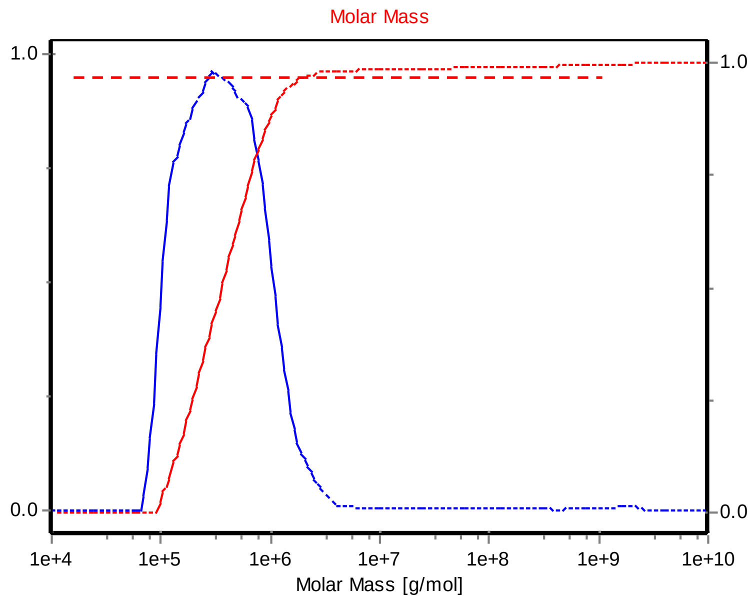
Conditions

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

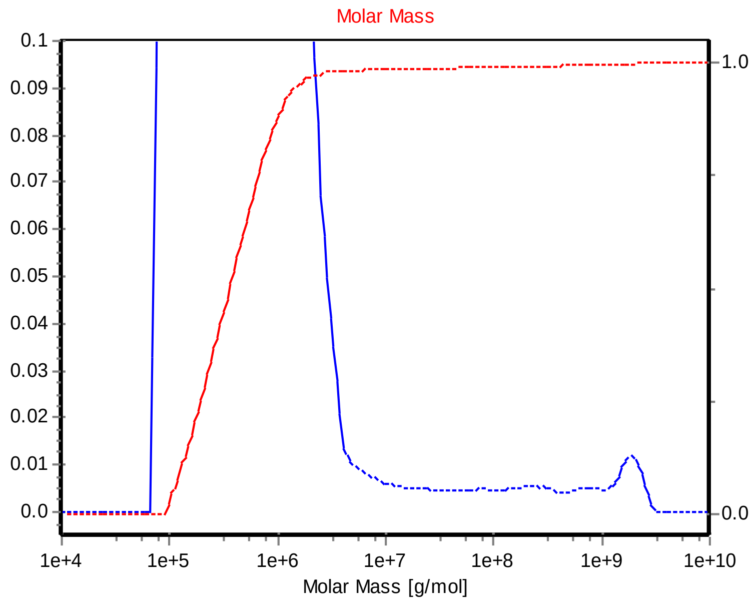
		R_g [nm]
1. Peak 13.0 – 48.5 min	*n*-Average	23
	w-Average	31
	***z*-Average**	**42**
2. Peak 48.5 – 56.0 min	*n*-Average	65
	w-Average	107
	***z*-Average**	**218**

TFFF Applications - Natural Rubber

Molar Mass Distribution



Zoom in Molar Mass Distribution

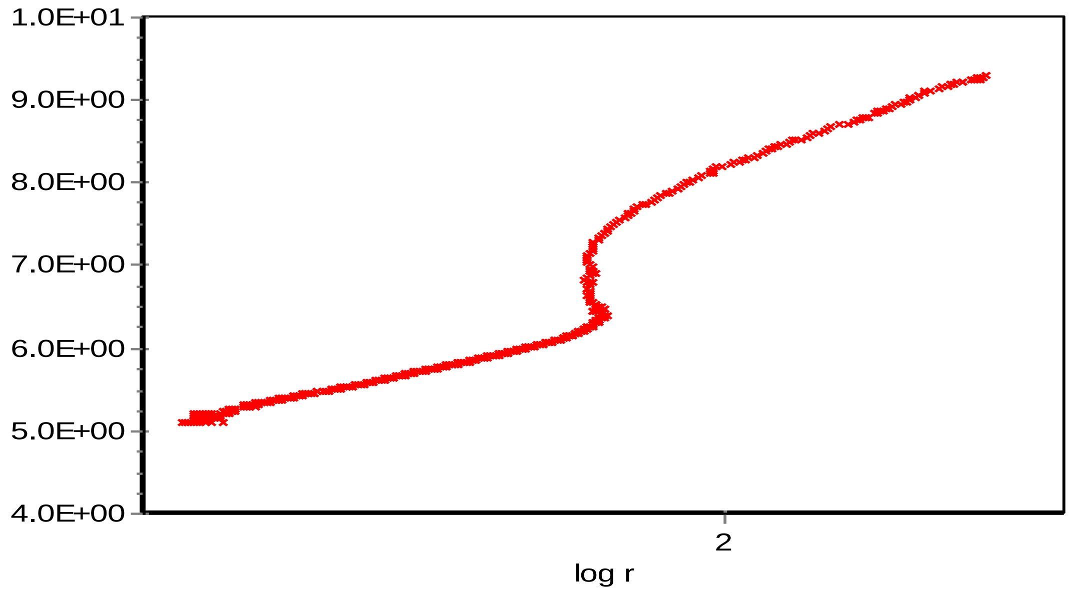


Differential Molar Mass Distribution (blue trace), Cumulative Molar Mass Distribution (red trace)

The sample shows a multimodal distribution. For the 1st fraction (13 – 48.5 min) the distribution is in the range of 9.2×10^4 – 2.8×10^6 g/mol and for the 2nd fraction (48.5 – 56 min) in the range of 2.7×10^6 – 2.3×10^9 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

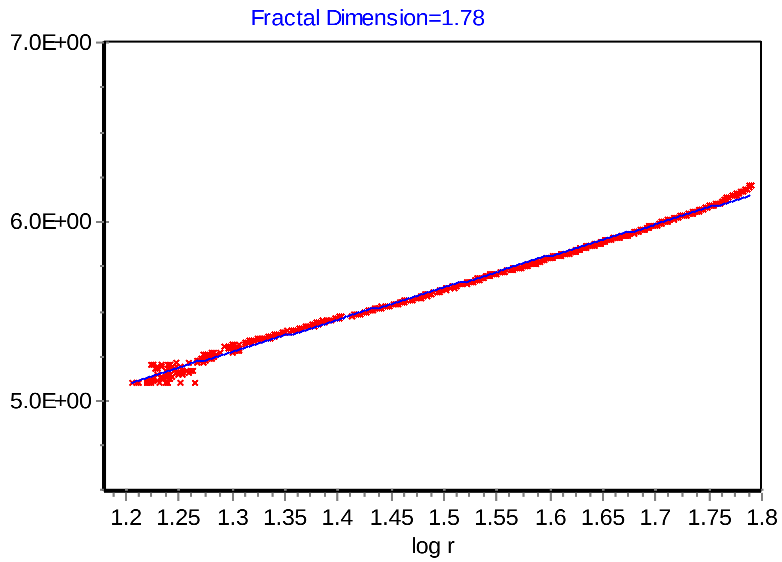
- PN5300 Auto Injector
- AF2000 FFF System
- PN3621 MALS Detector
- PN3150 RI Detector
- PN3510 ELSD

Conditions

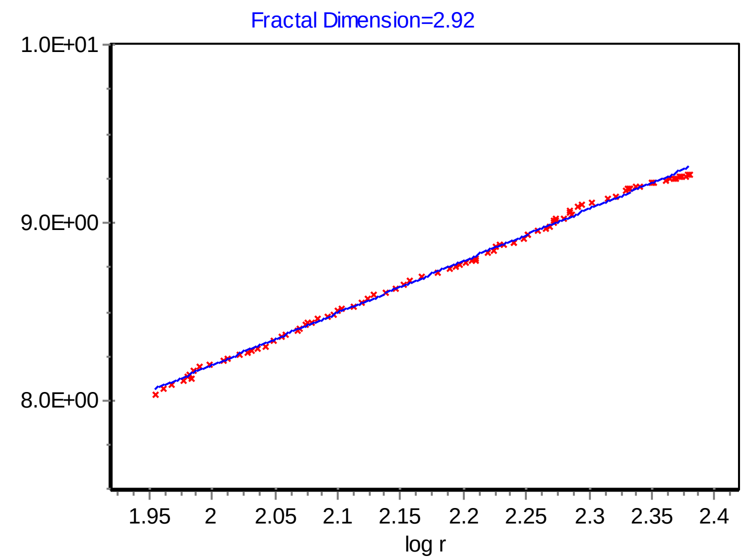
- Injection Volume: 20 µL
- Concentration: 2 mg/mL

TFFF Applications - Natural Rubber

Fractal Dimension 17.5 - 44.6 min



Fractal Dimension 51.6 – 54.8 min



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