

Characterization of SBR elastomer systems with GPC and FFF

20th September 2018, Wyatt

Structure

- Introduction: Where is Merseburg? What is the expertise of UAS Merseburg?
- Introduction to polymer characterization
- Insights into polymer properties of rubber materials due to
 - Field Flow Fractionation and
 - Light Scattering
- Hyphenated analytical techniques that yield superior understanding of polymer systems



Department of engineering
and natural sciences

Plastics competence centre Halle-Merseburg



Kunststoff-Kompetenz-Zentrum



Institut für
Polymerwerkstoffe e.V.



Polymer Service
Merseburg GmbH

Institute for
polymeric materials

About us - HoMe

University of Applied Sciences Merseburg

Education: Engineering and Natural Sciences

Chemical/Environmental Technology – B.Eng.

Chemical/Environmental Engineering – M.Eng.

Chemistry – B.Sc.

Mechanical Engineering / Mechatronics /

Physics Technology – B.Eng. & M.Eng.

Automatization/Information Technology – B.Eng.

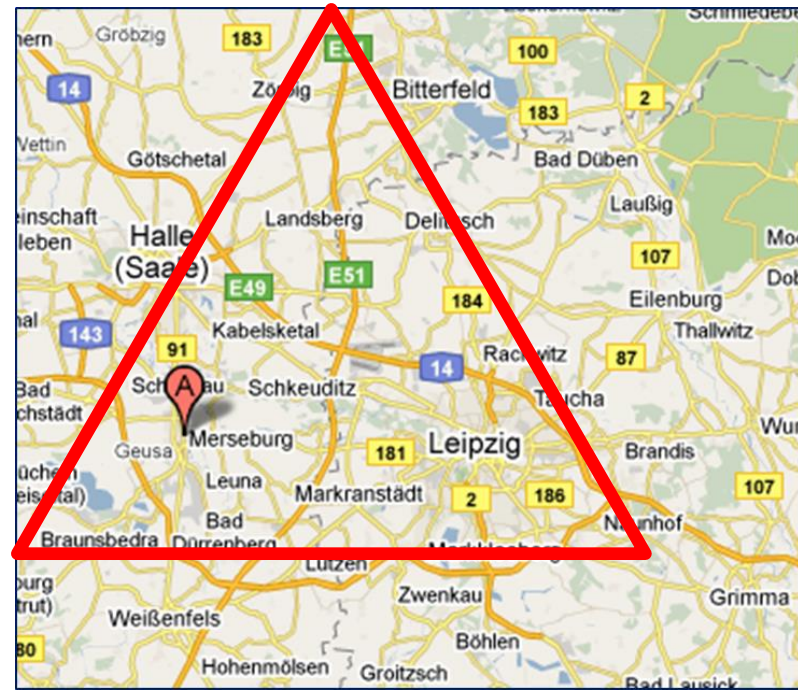
Economic Engineering – B.Eng.

Applied Informatics – B.Sc.

International Programs:

Engineering and Management - M.Eng., starts '19

Polymer Materials Science – M.Sc.



Located in the East German Chemistry

Triangle with 2,000 chemical companies, e.g.

Bayer, Dow, BASF, Total, Celanese...

Merseburg – about 2 hours to Berlin

by car or by train

Research: chemistry, polymers, raw materials, energy, protect. environment, sustainability

Prof. Dr. Valentin Cepus | Instrumental Analysis and Polymer Characterization

Introduction to polymer characterization

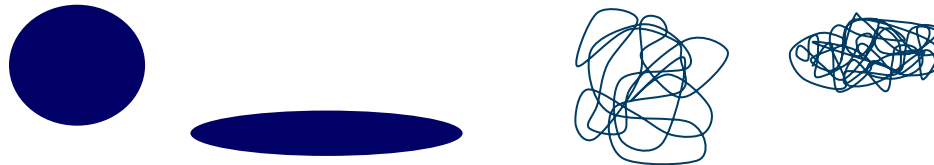
What's the difficulty of polymer characterization

- no exact structure formula
 - repeating elements – not necessarily monomer formula (copolymers)
 - there are always slight differences between individual polymeric chains
 - main components of synthetic polymers = polymeric chain
 - side components = additives, side products of the polymerization reaction, monomeric residues
 - the more precision is demanded the bigger the work
 - other demands for polymer analysis as in classical analysis
 - Absolute determinations are very difficult
 - Relative determinations, e.g. derived physical properties are often used: rheologic data, diffusion, permeability – **molar mass distribution**
 - works only well for homologueous systems
 - **constitution = sequences of atoms**
 - PVAc and PMA – equal sum formula, but different sequence
-
- configuration – stereoisomery
 - conformation – **geometric size and shape**



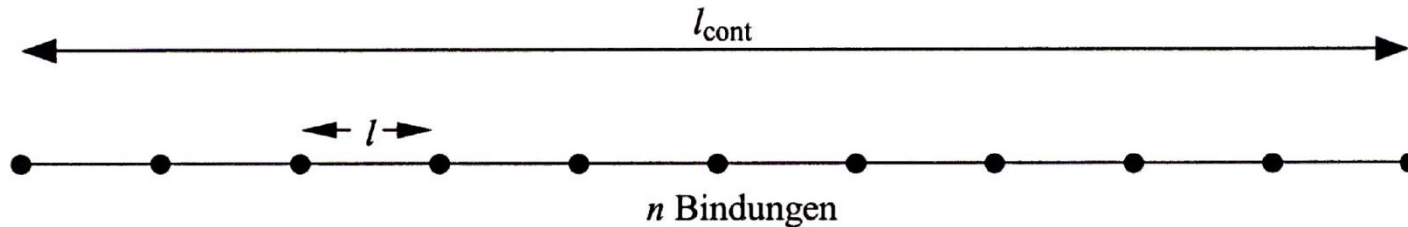
Geometric size and shape

- Multitude of possibilities of orientation of monomeric units
- Interaction of monomeric units with those of other polymeric chains and with other molecules (e.g. solvents)
- Outer shape
 - sphere
 - Rod
 - coil
 - Transitions between all named structures
- Geometric restrictions will favour one of the structures, e.g. rods
- Most abundant shape is the polymeric coil
- Also rod-like molecules converge for large M to coils
- Geometric parameters show a distribution like molar mass does
- Averages of geometric parameters are dependent on the principle of measurement (light scattering z-average and n-average; viscosimetry w-average)

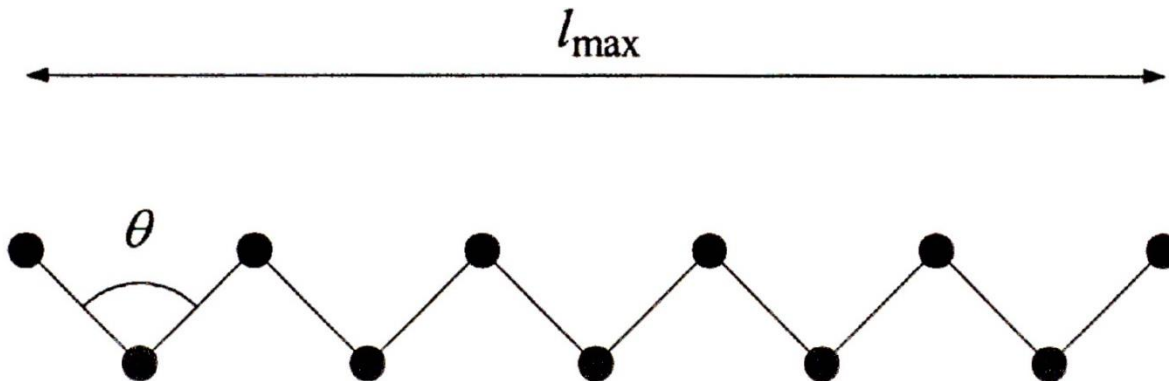


Polymers in solution

- free rotating chain
- **contour length** l_{cont} is the total length of the chain $l_{\text{cont}} = n l$
 n = number of bonds l = Length of bond



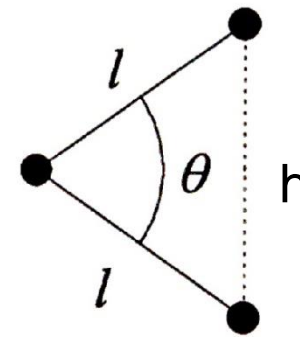
- **maximal chain length** $l_{\text{max}} = n l \sin(\theta/2)$



from: Tieke

Polymers in solution

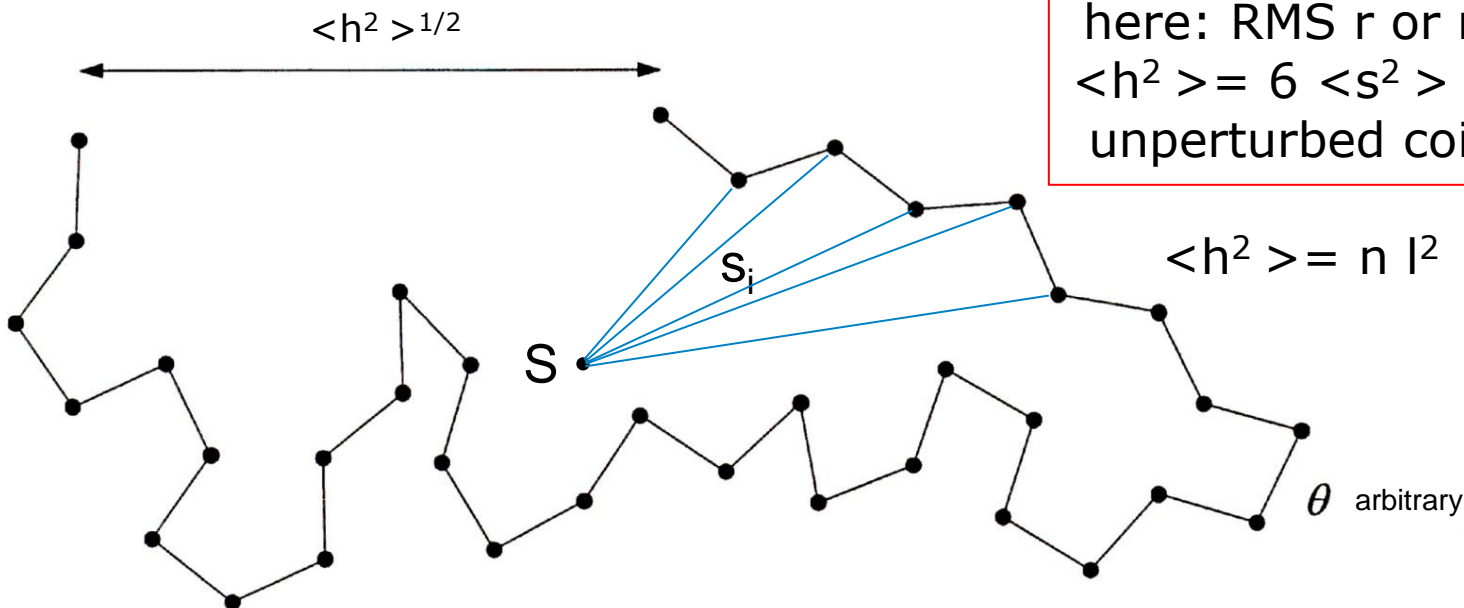
- **Average chain end to end distance** $\langle h^2 \rangle^{1/2}$
 - $h^2 = 2 l^2 (1 - \cos \theta)$
 - h^2 becomes $\langle r^2 \rangle$ (in the average)
 - Because all angles are possible:
 $\langle \cos \theta \rangle = 0, \Rightarrow \langle h^2 \rangle = 2 l^2$



- **For n segments:** $\langle h^2 \rangle^{1/2}$
 - h^2 becomes $\langle h^2 \rangle$ (in the average)
 - Shortened by coiling $\Rightarrow \langle h^2 \rangle = n l^2$

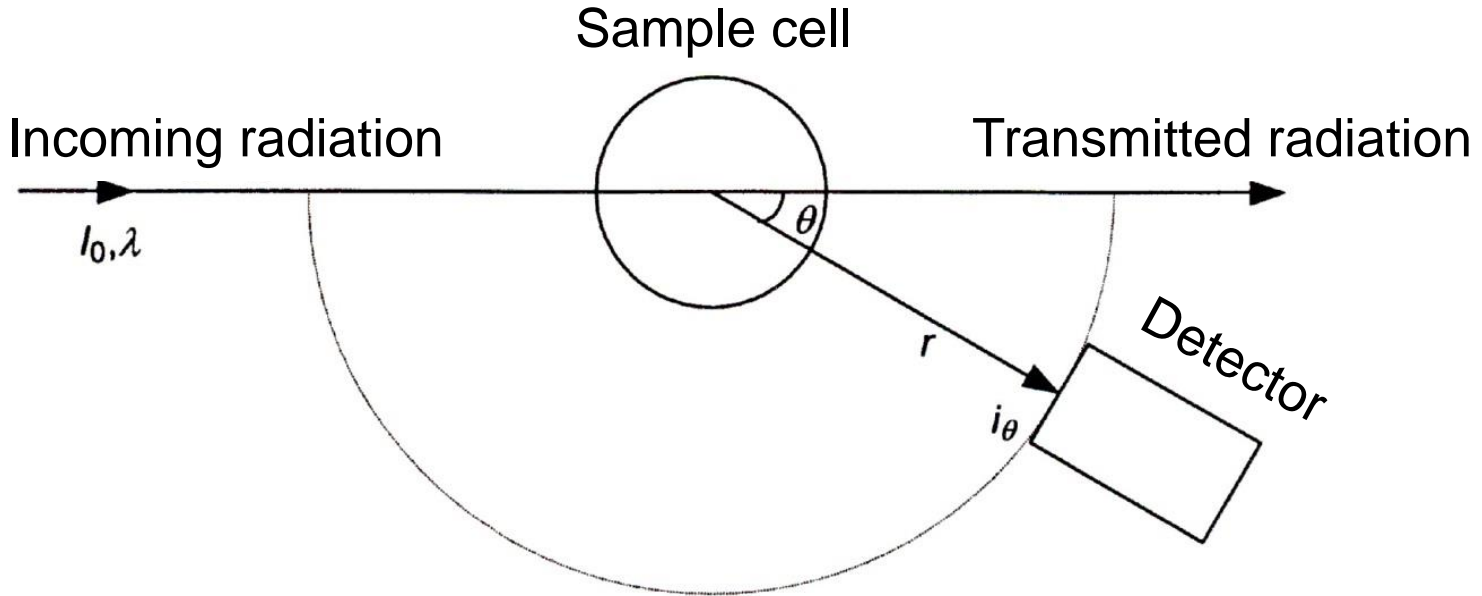
radius of gyration: $\langle s^2 \rangle^{1/2}$

average of the distance from center S to chain
 here: RMS r or r_g
 $\langle h^2 \rangle = 6 \langle s^2 \rangle$ for unperturbed coil



from: Tieke

Light scattering - determination of molar mass



- The intensity of the scattered radiation is dependent on the angle
- At an angle θ the scattering intensity i_θ is defined as reduced scattering intensity R_θ (Rayleigh ratio)

$$R_\theta = \frac{i_\theta \cdot r^2}{I_0}$$

- r =distance between scattering sample and detector

Light scattering - determination of Mw

- According to Rayleigh's theory of light scattering:

$$R_{\theta} = \frac{4 \cdot \pi^2 \cdot n_0^2}{\lambda^4 \cdot N_A} \cdot \left(\frac{dn}{dc} \right)^2 \cdot c \cdot M \cdot f \cdot p$$

n_0 = refractive index of the solvent
 dn/dc = refractive index increment of polymer solution

c = concentration of the polymer solution

f = depolarisation factor (Carbannes factor) ca. 1

p = polarisation factor = $(1 + \cos^2 \theta)/2$ for unpolarized light and ca. 1 for vertically polarized light

- To be combined in one constant:
- There is a remaining dependence of c and M :
- From the definition of M_w follows

$$K = \frac{4 \cdot \pi^2 \cdot n_0^2}{\lambda^4 \cdot N_A} \cdot \left(\frac{dn}{dc} \right)^2$$

$$R_{\theta} = K \cdot c \cdot M$$

$$R_{\theta} = K \cdot \sum c_i \cdot M_i = K \cdot c \cdot M_w \quad \text{or}$$

$$\frac{K \cdot c}{R_{\theta}} = \frac{1}{M_w}$$

Light scattering – large molecules

- The occurrence of the internal interference do also contain information about the size and shape of the polymer molecule
- The particle scattering factor depends on the size and form of the polymer and on the wavelength
- For a coil the particle scattering factor is:

$$\frac{1}{P(\theta)} = 1 + \frac{16\pi^2 \langle s^2 \rangle}{3\lambda'^2} \sin^2 \frac{\theta}{2} \quad \text{mit} \quad \begin{array}{l} \lambda' = \lambda/n_0 \\ \langle s^2 \rangle = \text{square of the} \\ \text{average radius of} \\ \text{gyration} \end{array}$$

- Combining this with the equation on the previous slide:

$$\frac{K \cdot c}{R_\theta} = \frac{1}{M_w} \left(1 + \frac{16\pi^2 \langle s^2 \rangle}{3\lambda'^2} \sin^2 \frac{\theta}{2} \right) + 2A_2 \cdot c$$

- By measurement of the light scattering at different angles and concentrations M_w , $\langle s^2 \rangle^{0,5}$ and A_2 can be determined

Innovative methods for polymer characterization

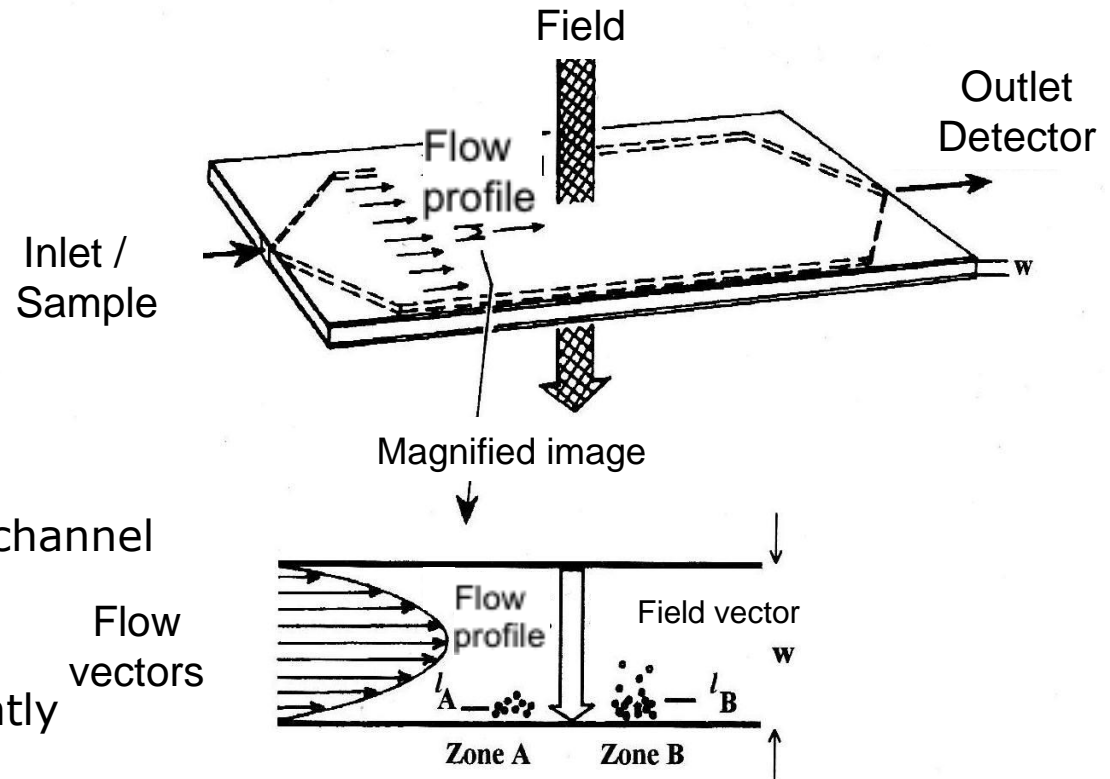
Field flow fractionation

2D-HPLC-GPC

Field flow fractionation with UV/VIS, RI, and light scattering detection

FFF – field flow fractionation

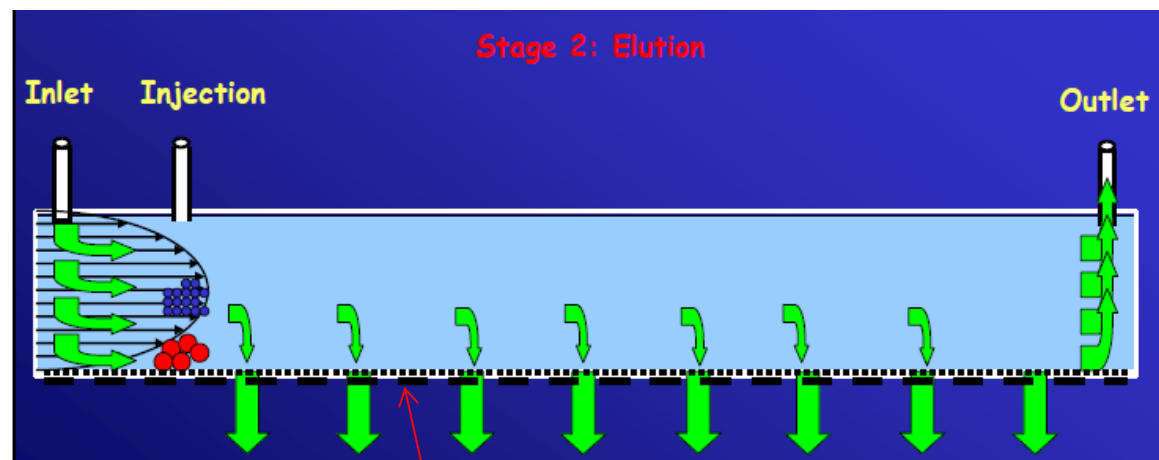
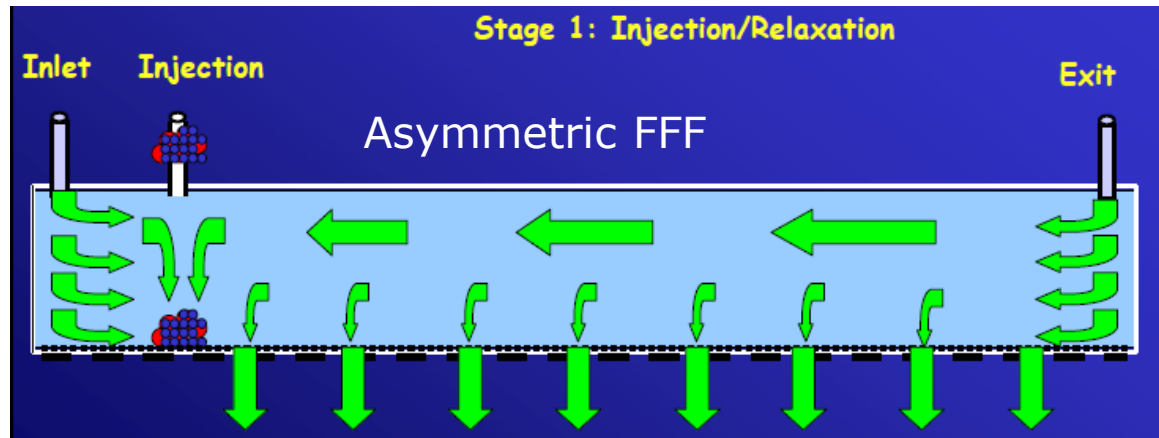
- molar mass of very large polymers and disperse systems
- Principle: Separation of molecules and disperse systems in a channel
- perpendicular disturbing field
- e.g. semipermeable membrane built in the lower side
- Cross flow
- AF4 = asymmetric flow field flow fractionation
- Small molecules diffuse faster back to the centre of the channel = faster transport
- Large molecules are predominantly located near to the lower side = slower transport



From: Arndt, Polymercharakterisierung

FFF – field flow fractionation

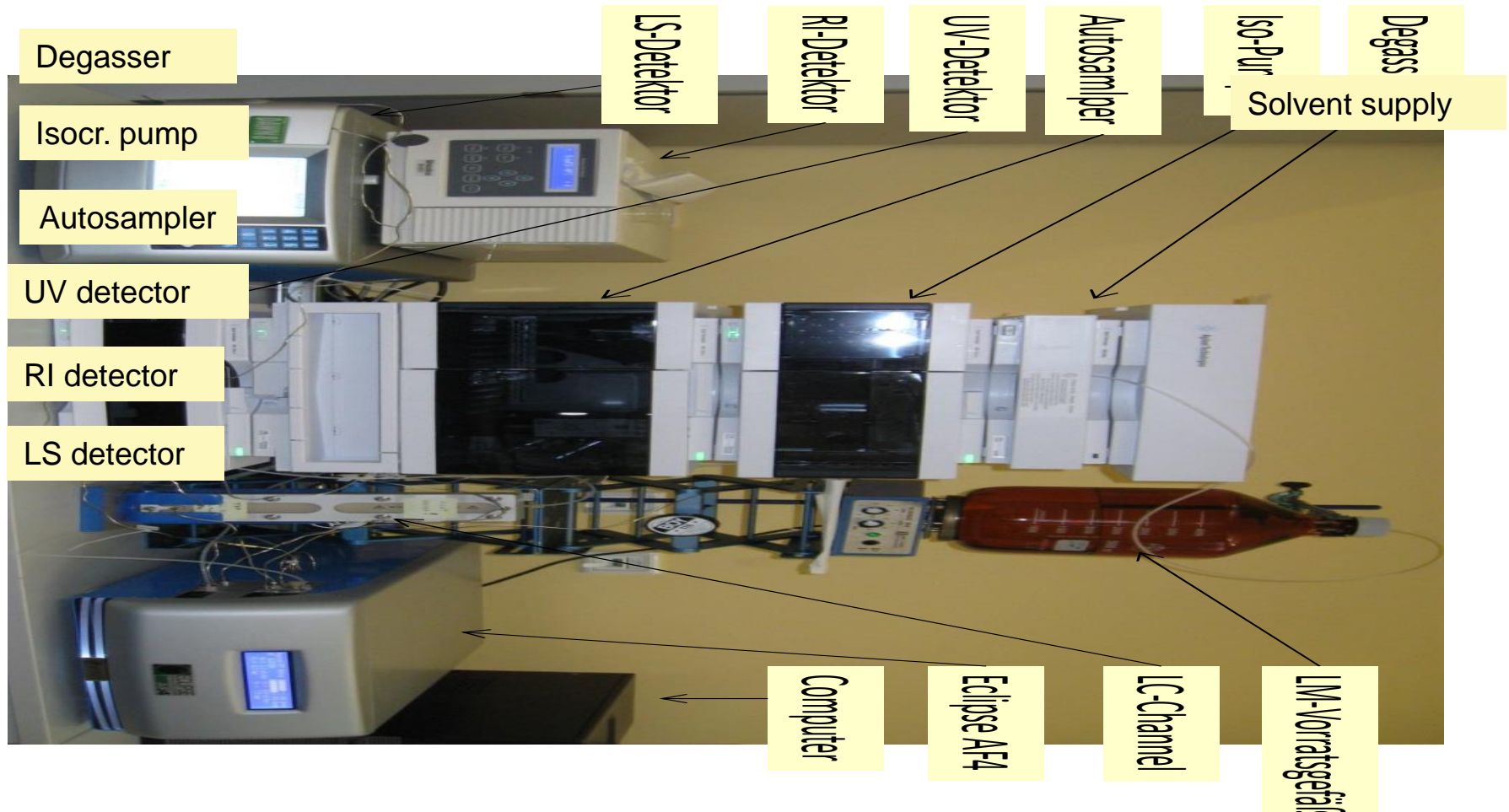
- separation of macromolecules in an open flow channel
- horizontal flow of the sample and perpendicular flow contribution of eluent
- small molecules with fast diffusion are mostly focused in regions of maximum flow
- larger molecules migrate more slowly in the laminar flow and will be eluted at a later point of time
- very mild method for sensitive macromolecules and also systems with particles



Semipermeable membrane
from: Wyatt

FFF – field flow fractionation

- set-up of the instrument



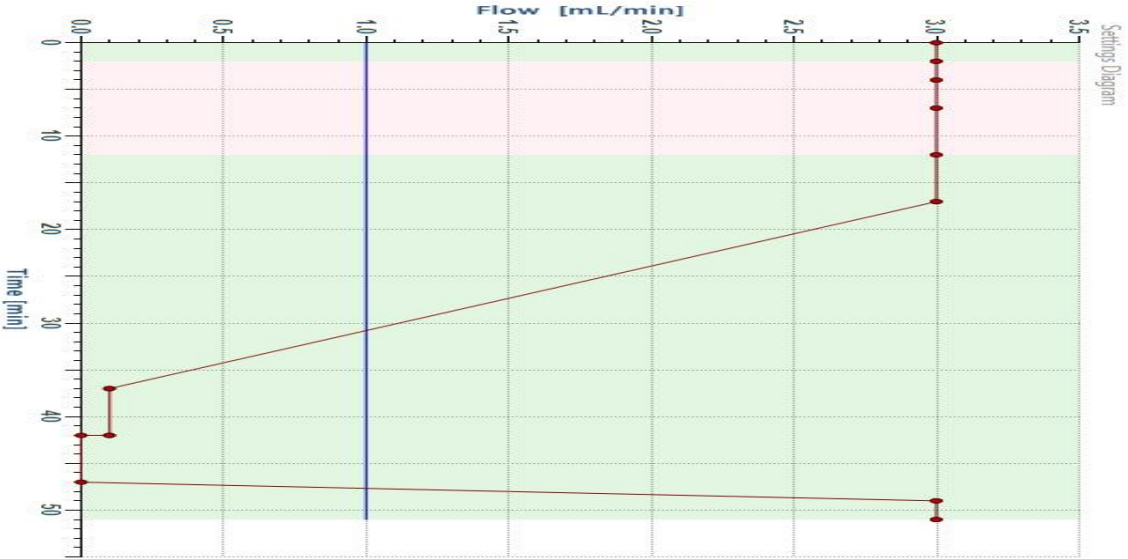
FFF – Field flow fractionation – method development

Crossflow
(Cf in
ml/min)

ECLIPSE® Method

Time table

Mode	Duration [min]	Cross Flow Start [ml/min]	Cross Flow Stop [ml/min]	Flow Profile
Elution	20	3.00	3.00	Constant
Focus	20	3.00	3.00	Constant
Focus Inject	30	3.00	3.00	Constant
Focus	50	3.00	3.00	Constant
Elution	50	3.00	3.00	Constant
Elution	200	3.00	0.10	Linear
Elution	50	0.10	0.10	Constant
Elution	50	0.00	0.00	Constant
Elution	20	0.00	3.00	Linear
Elution	20	3.00	3.00	Constant



Insert

Append

Delete

Clear

Default

Flow Settings

Detector Flow

1.00

ml/min

Inject Flow

0.00

ml/min

Separation Device

LC-A

Membrane Type

RC5 KD8

Pressure Limit [bar]

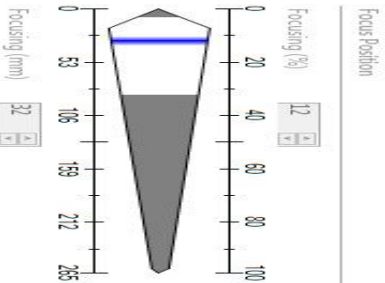
30.0

Spacer Height [µm]

350

Spacer Type

W



Solvent and Membrane Settings

Solvent

Tetrahydrofuran

Required Volume [mL]

142.50

Temperature [°C]

25.0

☐ Focus Shift enabled

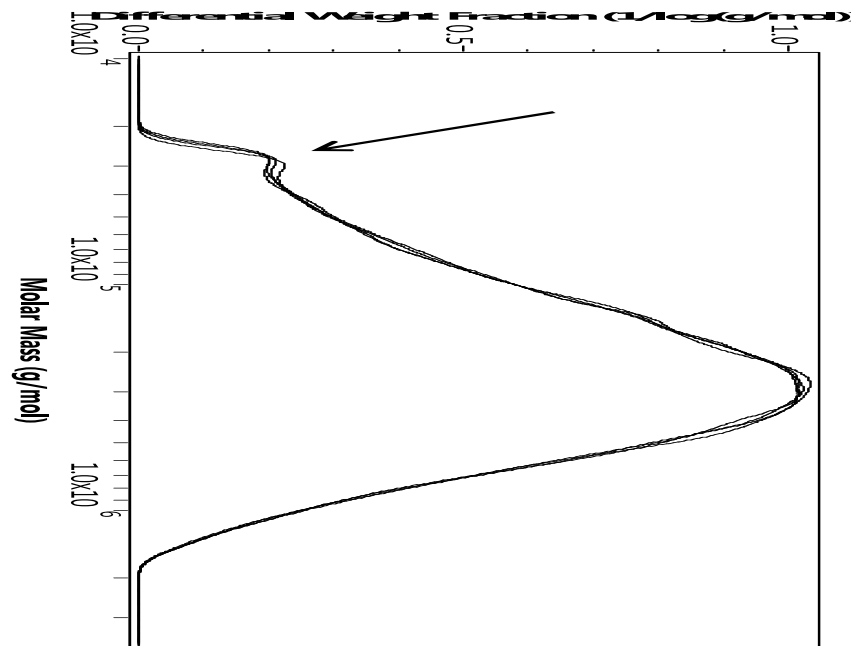
Apply to All

Apply

Reset

FFF – reference example – polystyrene

- Limitations towards low molar masses – upswing in curve due switch to elution
- Close match to reference values
- low standard deviations



Vorgabe-Werte:
Mn: 170kDa
Mw: 350kDa

PS Sigma 441147 Mn (kDa) Mw (kDa) Mw/Mn η (cm)

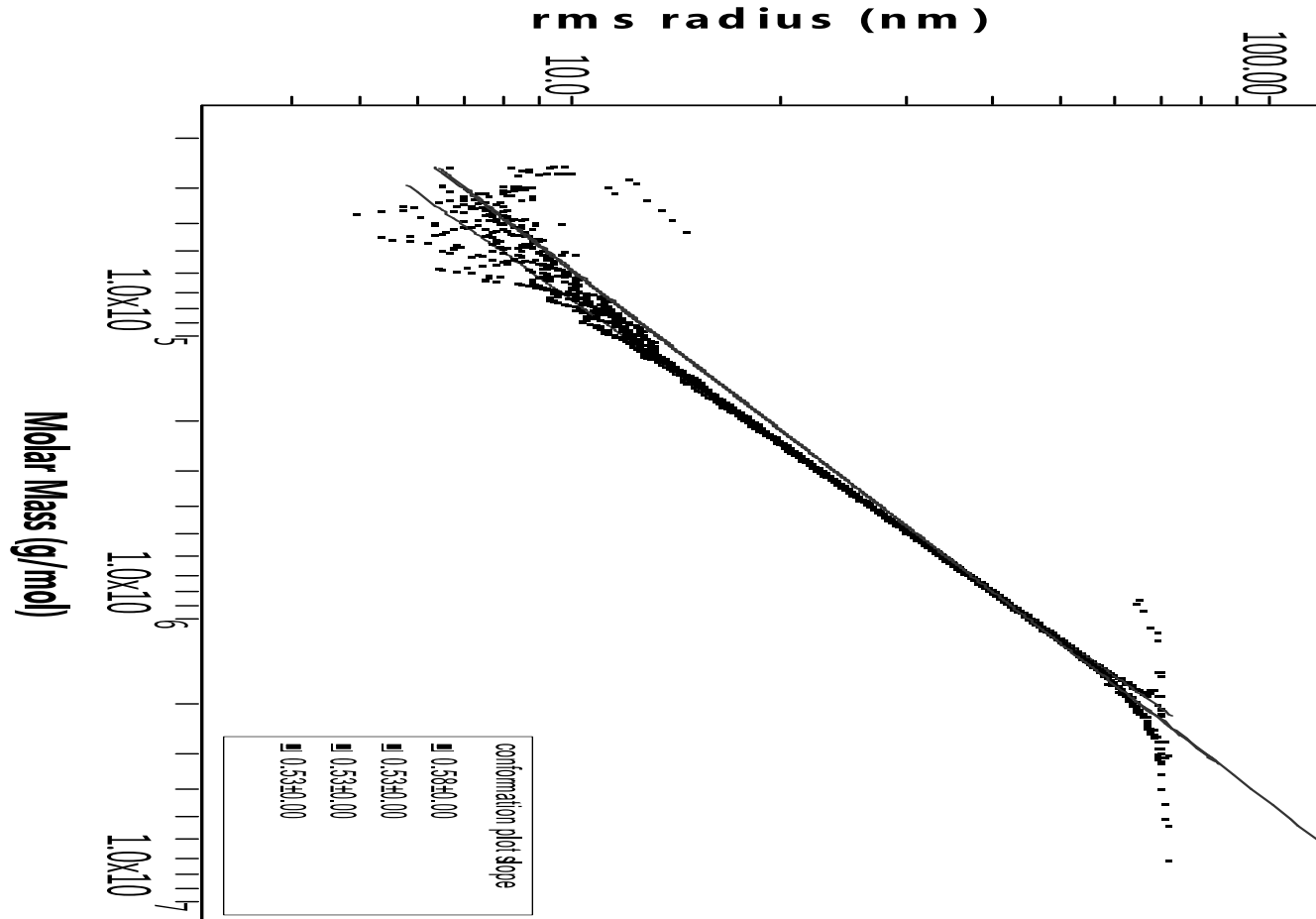
RI 04 025 841147 LC-A	141.2	308.7	2.187	32.4
RI 04 025 841147 LC-A	145.3	314.9	2.177	32.5
RI 04 025 841147 LC-A	143.9	313.9	2.17	32.5
RI 04 025 841147 LC-A	142.8	313.0	2.19	32.5

Average	143.3	312.6	2.18	32.5
% Standard deviation	1.2	0.9	0.1	0.1

Reference values

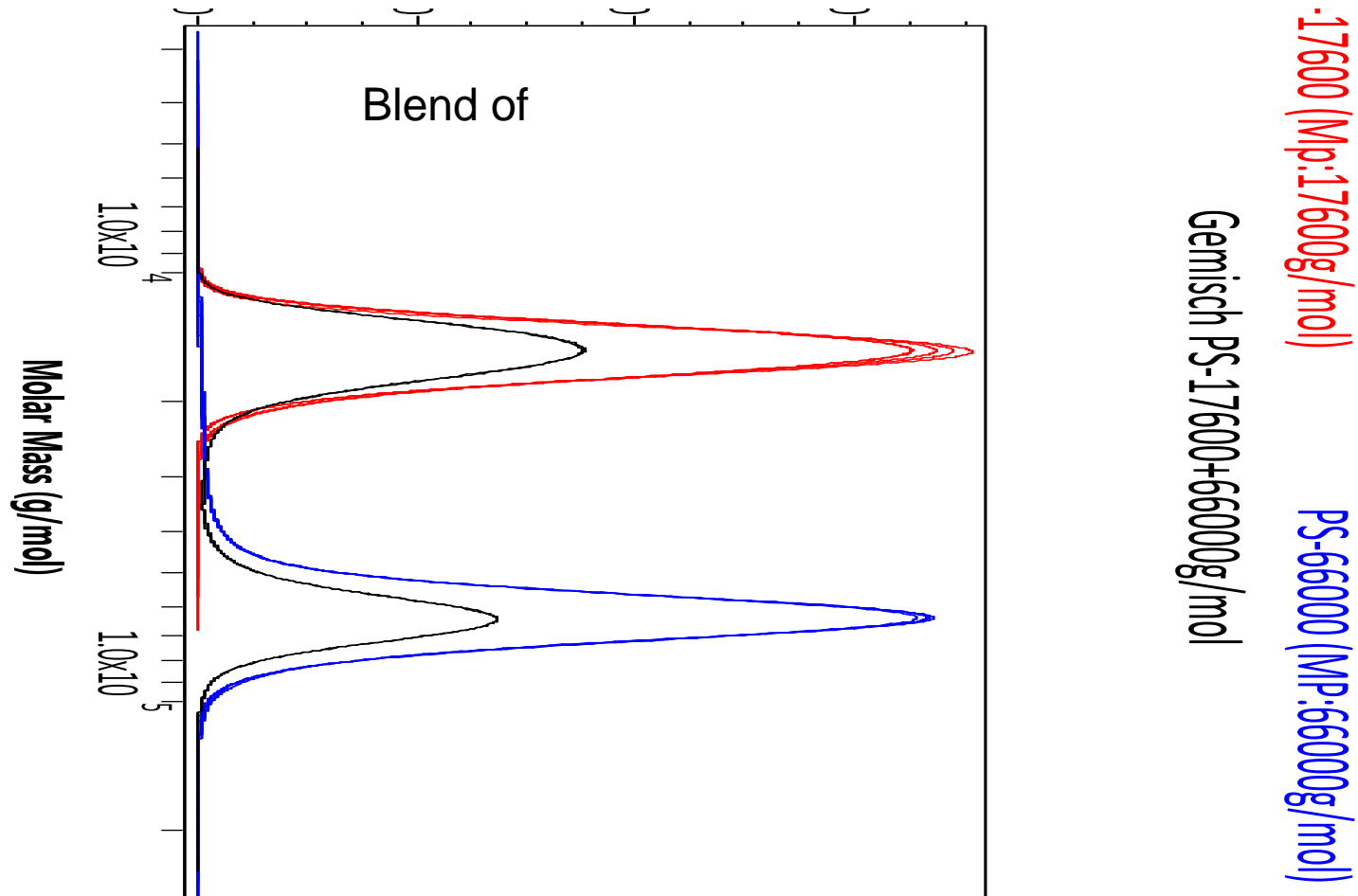
FFF – reference example – polystyrene

- Theory – shape prediction by slope in conformation plot: 0.33 – sphere; 0.50 random coil; 1.00 - rod
- conformation plot shows slope of around 0.55 - regular statistic coil



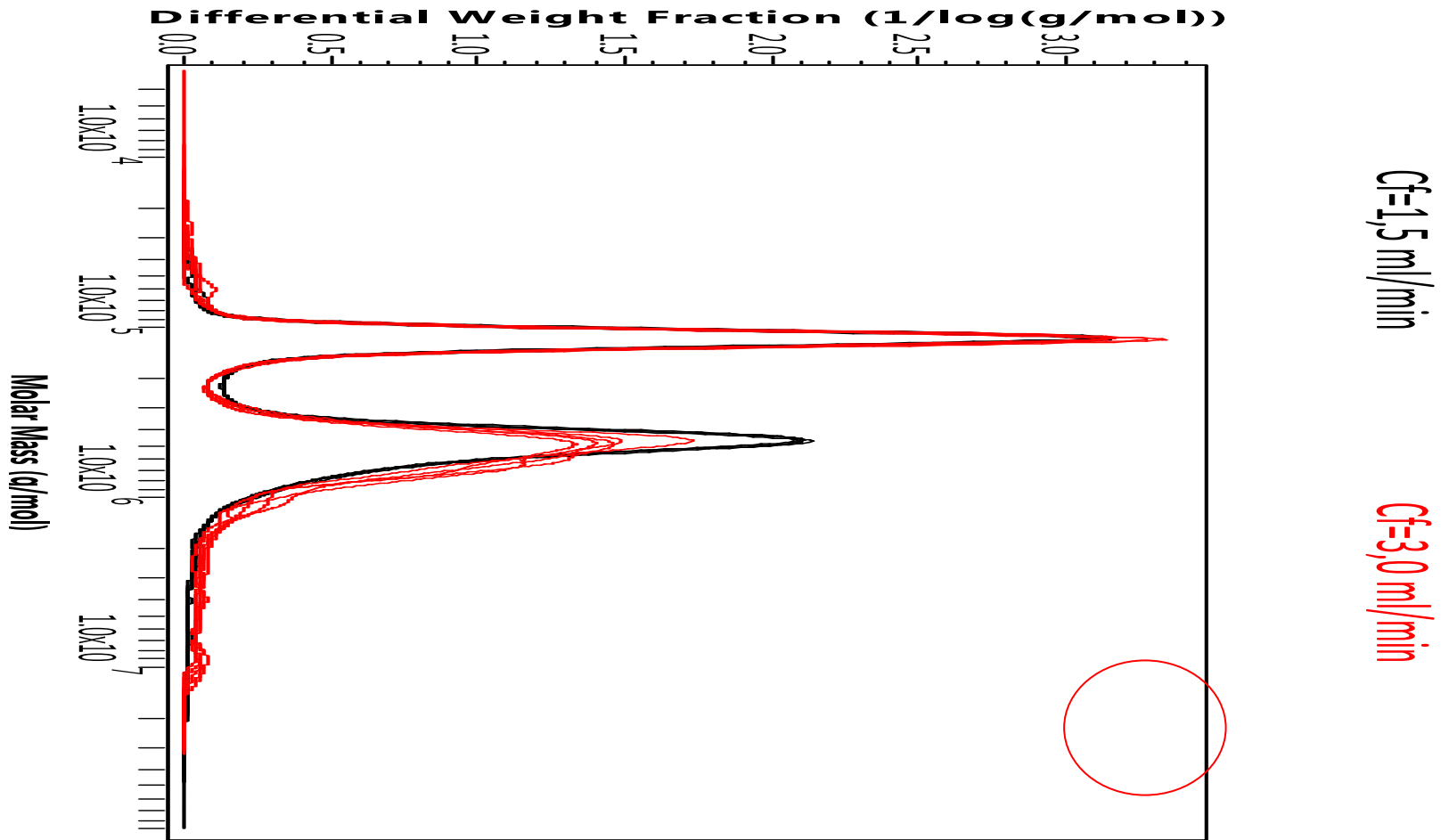
FFF – reference example – polystyrene blend

- blend of two PS samples with narrow molar mass distribution
- very good match to reference values



FFF – rubber samples #1

- blend of rubber materials
- similar amount of low and high M rubber material

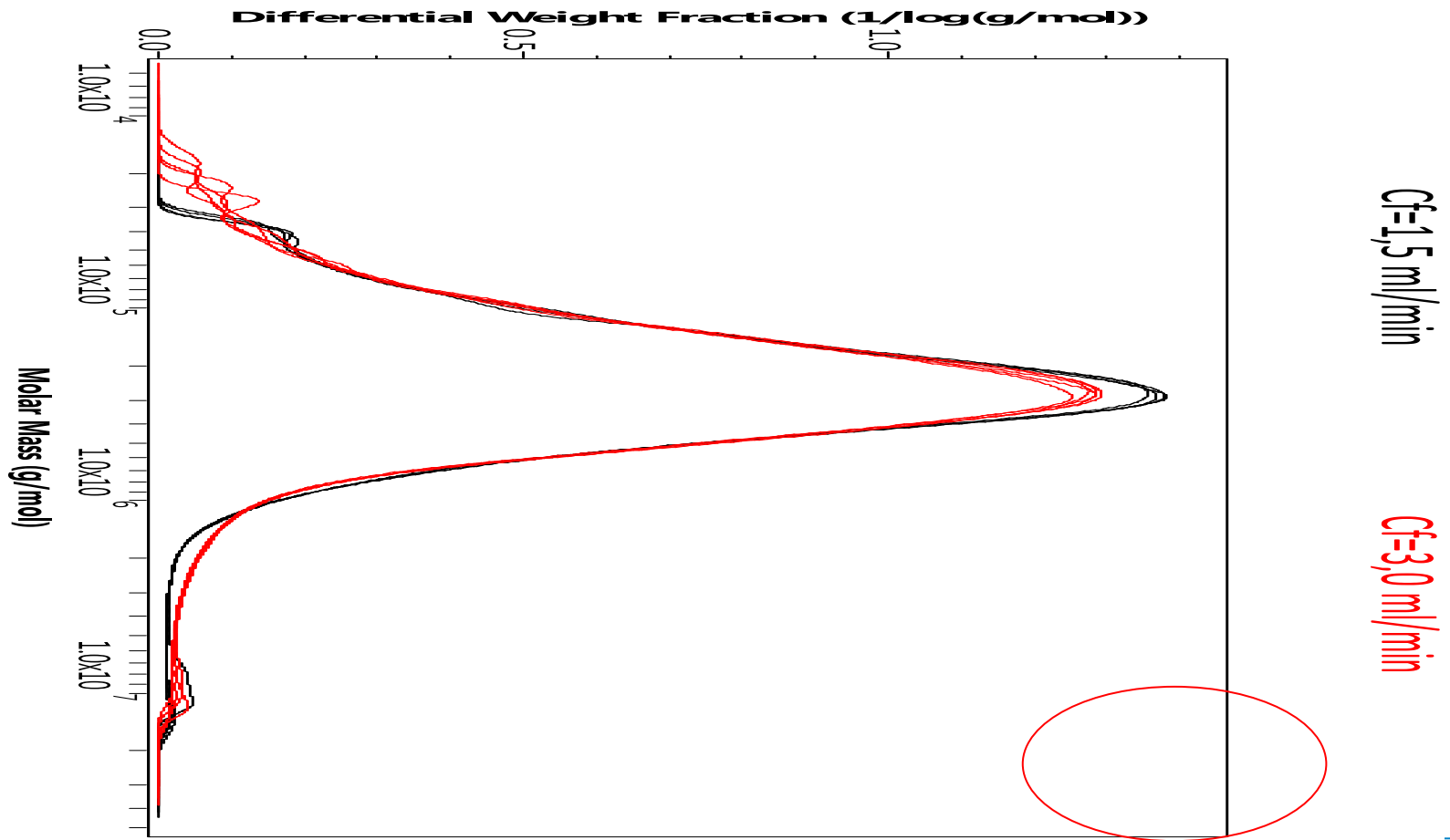


- low M fraction of rubber $2 - 5 \times 10^5$ to 10^6 Da – slope of 0.5
- higher M fraction of rubber with slope of 0.4 to 0.5 – denser coil



FFF – rubber samples #2

- rubber material with low amount of high M rubber
- hard to see with GPC



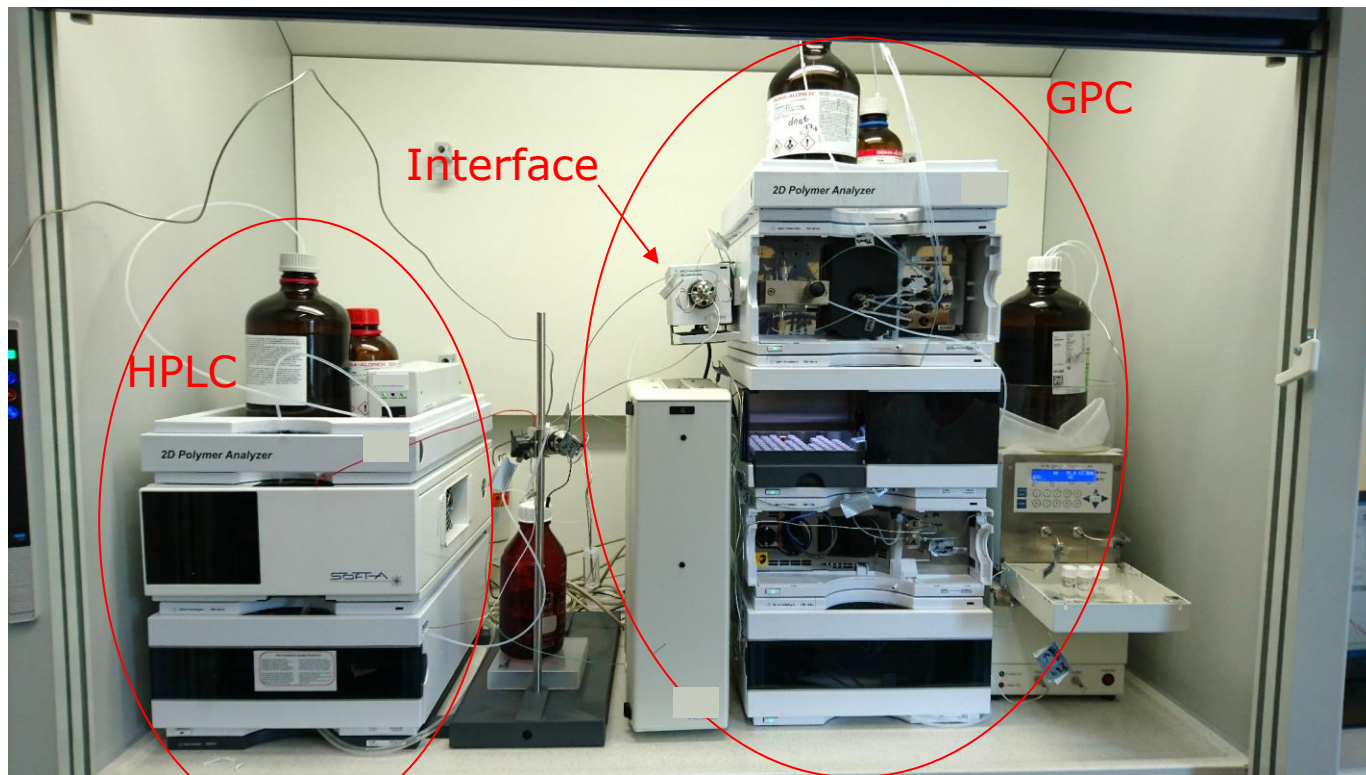
- main fraction of rubber between 10^5 to 10^6 Da – slope of 0.6 to 0.65
- side fraction of rubber at very high M_w – slope of 0.03 to 0.1 – much denser



Hyphenated analytical techniques that yield superior understanding of polymer systems

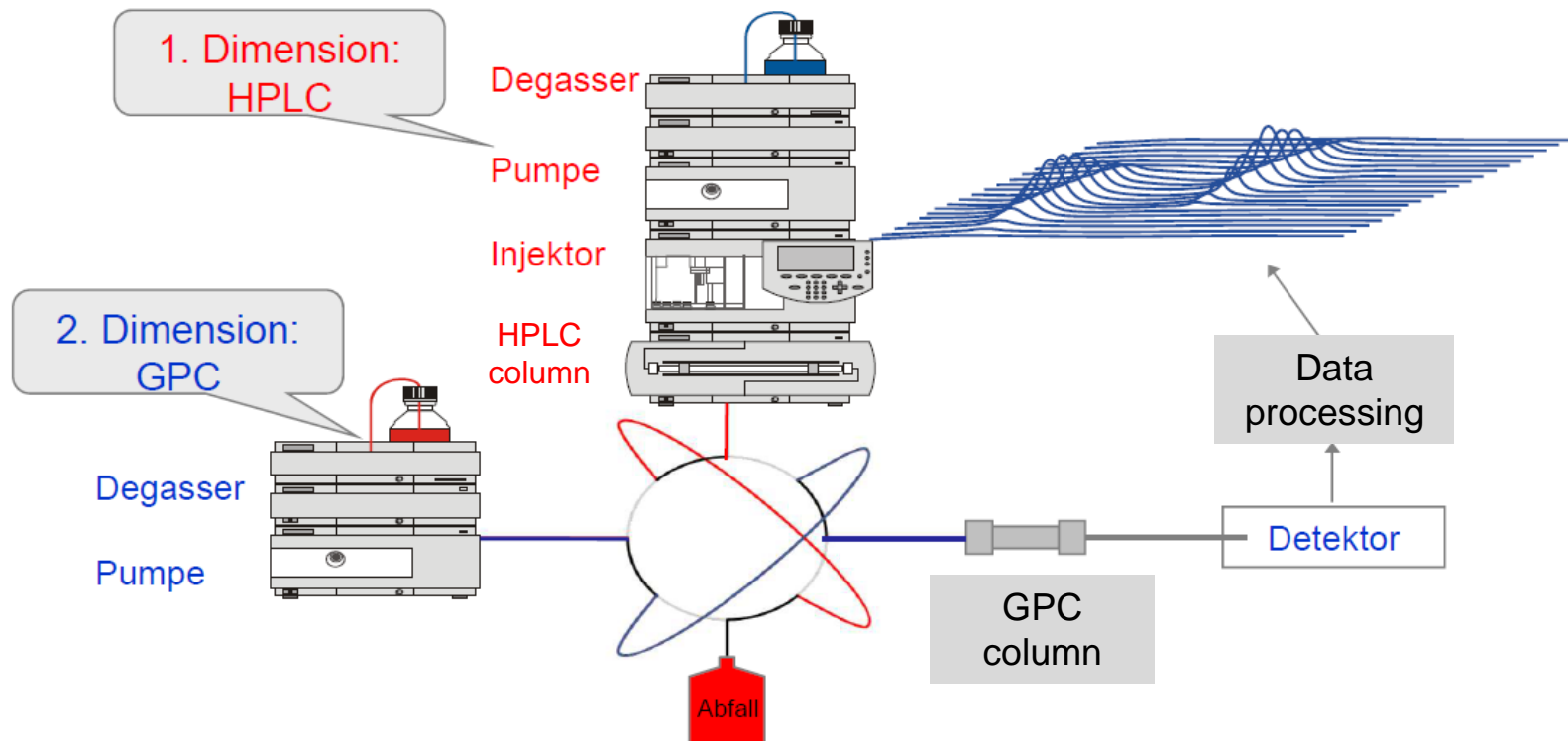
2D HPLC GPC coupling

- Separation mechanism of GPC: hydrodynamic volume
 - Distribution of molar mass of chemically homogeneous polymer samples
- No sensitivity towards the chemical composition
- Separation acc. to the chemical composition by preceding HPLC (prior to GPC)



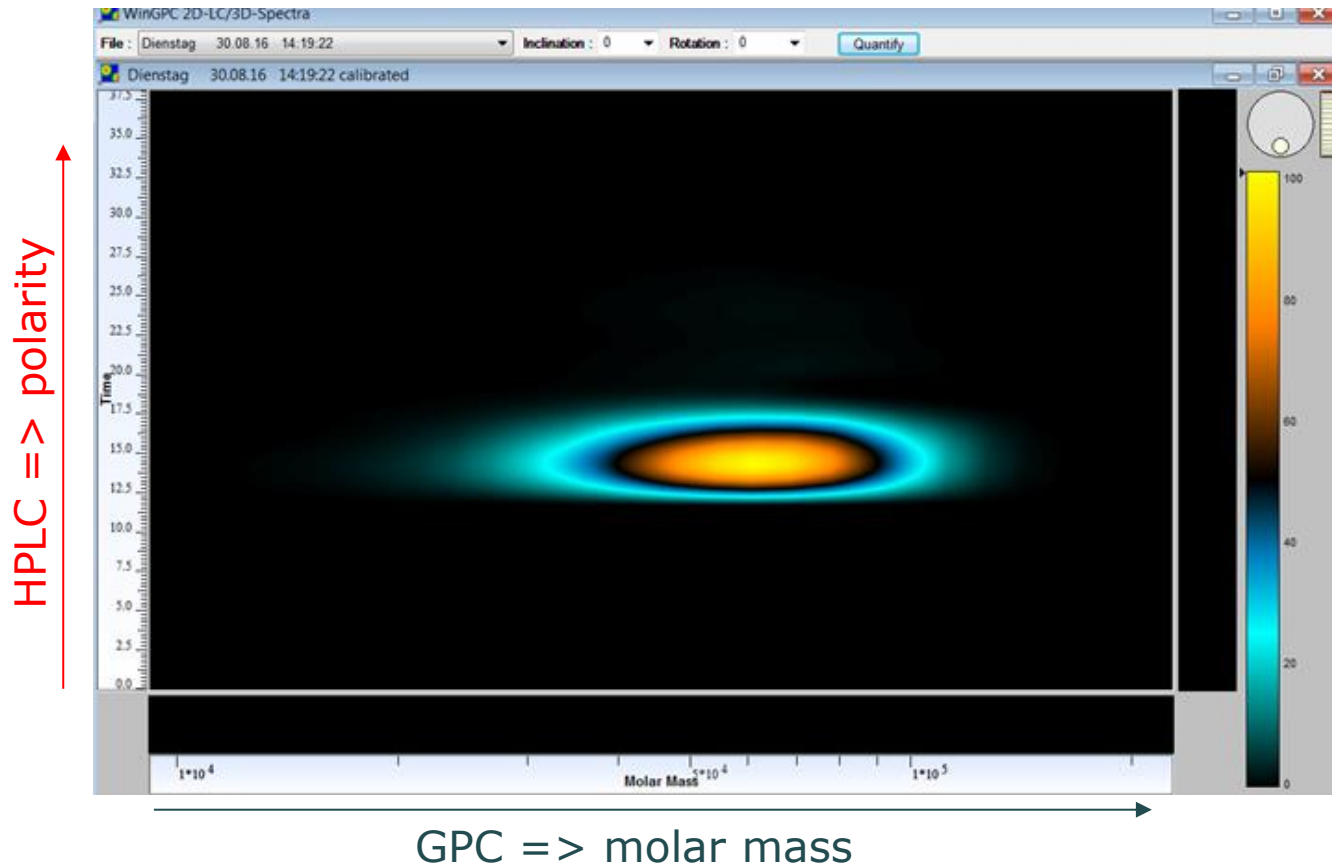
2D HPLC GPC coupling

- Switch valve with two sample loops serves as a transfer valve
- Separation in the HPLC => Eluate is collected in one of the sample loops
- Simultaneously the content of the second samples is separated and analyzed by GPC



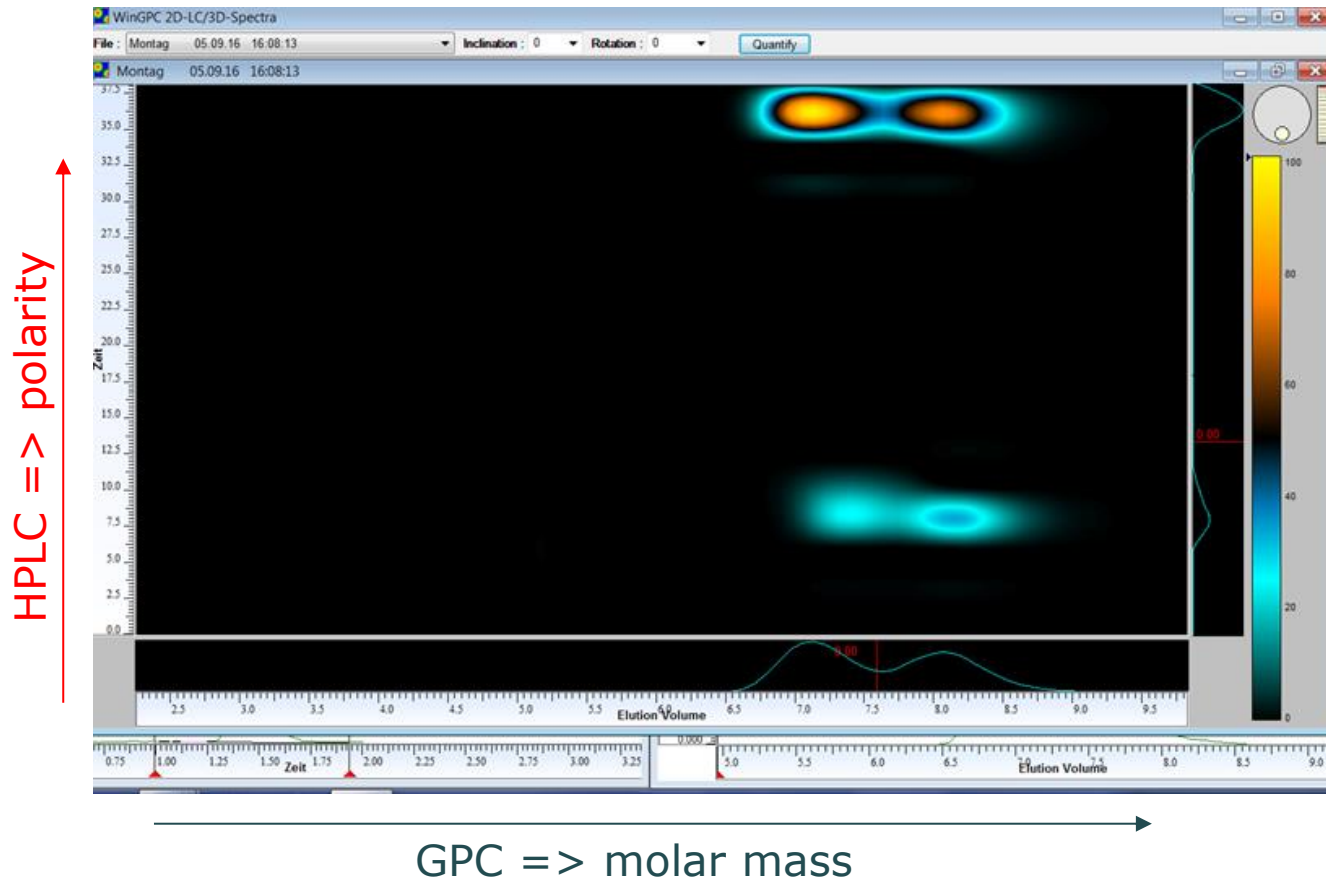
2D HPLC GPC coupling – first results

- Y axis shows HPLC separation - polarity
- X axis shows GPC separation – molar mass
- Simple case: PS-PMMA block copolymer = one copolymer with intramolecular mixture of polarity and a monomodal distribution of the molar mass



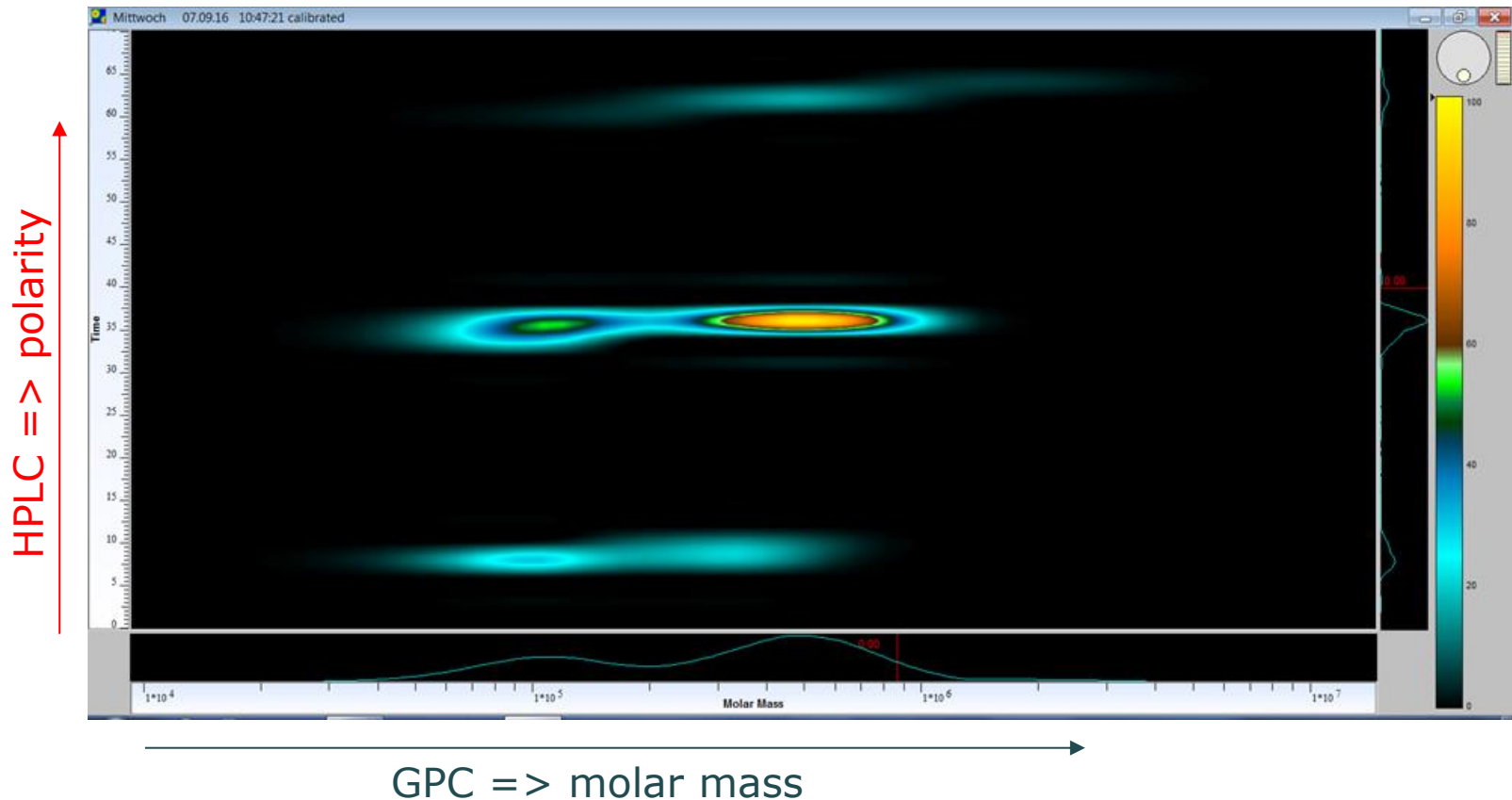
2D HPLC GPC coupling – first results

- Mixture of 2 PS homopolymers and 2 PMMA homopolymers with narrow distribution of molar mass
- 4 peaks can be identified, in spite of similar molar mass



2D HPLC GPC coupling – first results

- Mixture of 2 PS homopolymers and 2 PMMA homopolymers with narrow distribution of the molar mass plus 1 polybutadiene
- 5 Peaks can be identified, in spite of similar molar mass, distribution of PB broader



Summary

- Determination of **molar mass distribution** and **shape** parameters are important for the characterization of polymer systems
- FFF with LS detection offers a powerful tool for both of these aspects
- Results for innovative rubber systems provide complementary characterization results added to SEC results for research partners from rubber industry
- Hyphenated 2D LC methods with HPLC and SEC polymer separation can differentiate polymer blends, e.g. obtained by side-chain functionalization

Team polymer characterization @ UAS Merseburg:

Dr. Sven Poser, Petra Brose, Liane Aue, Carsten Schicktanz, Sergei Wittchen,
Jan Klapproth, Rona Hohlfeld, Dr. Willi Frank,
Prof. Dr. Valentin Cepas

Thank you for your attention!