# Comprehensive Characterization of Macromolecules by Chromatography

Part I **Advanced SEC Separation and Detection**

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1. Introduction into SEC
2. Separation and 2D Chromatography
3. Detection and Information Content
4. Summary

Part II **FFF and Light Scattering**

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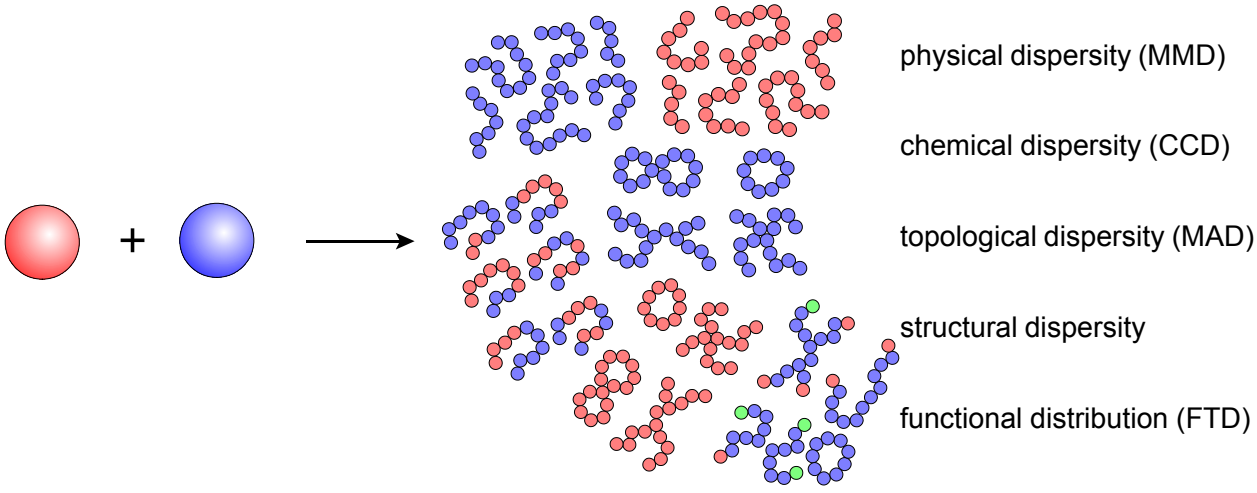
# Introduction

**Most polymeric materials are highly complex multi-component materials**

**even simple polymerization leads to products with multiple property distributions**

**Analytical Challenges: Determination of distributed properties**



physical dispersity (MMD)

chemical dispersity (CCD)

topological dispersity (MAD)

structural dispersity

functional distribution (FTD)

# Introduction

## Characterization Strategy

**A) Characterization of bulk materials** — **access to bulk properties / property averages**

requires batch methods

**e.g. Light Scattering (LS), Viscometry, Osmometry, Ultracentrifugation (AUC) NMR, IR, ...**

**B) Characterization of separated fractions** — **access to property distributions**

requires comprehensive chromatography

1) analytical fractionation methods: E.g. Liquid chromatography (GPC, LAC, LCCC)
Ultracentrifugation (AUC)
Field flow fractionation: FFF
(Gas chromatography: GC)
Mass sprectrometry: MALDI-ToF

2) detection techniques: e.g. RI, UV, LS, Viscometry, FTIR, NMR, MS

separation - detection combinations determine which distributions can be measured



# Introduction

## Chromatographic Modes

a) Size exclusion mode: SEC

$K_{SEC} = \exp(\Delta S/R)$

$0 < K_{SEC} < 1$ $\Delta H = 0$

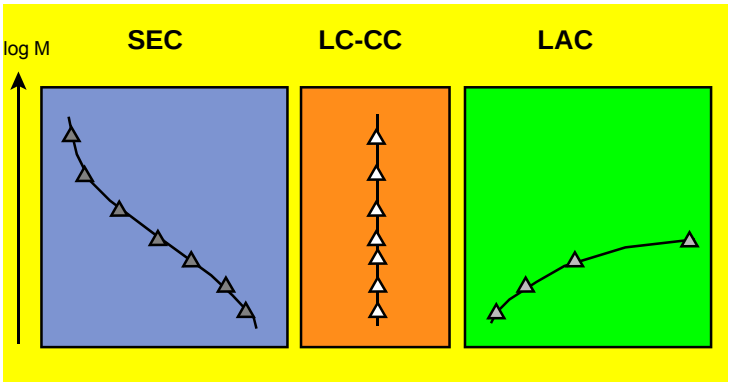
b) Adsorption mode: HPLC

$K_{HPLC} = \exp(-\Delta H/RT)$

$K_{HPLC} > 1$ $\Delta H \gg T\Delta S$

c) critical adsorption point: LC-CC

$K = 1$ $\Delta H = \Delta S$



# Chromatographic Modes of Separation

## Comparison of Chromatographic Modes

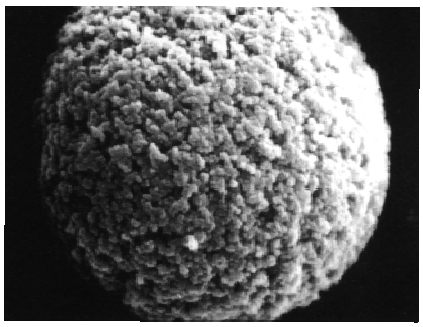
| technique | separation governed by | information content | potential problems |
|---|---|---|---|
| SEC | • hydrodynamic volume<br>• molecular size in solution<br>*diffusion controlled process* | • molar mass (MMD)<br>• chemical composition (CCD) | • calibration dilemma<br>• specific interactions |
| LC-CC | • chain inhomogeneity<br>• defect structures<br>• endgroups<br>*diffusion and adsorption controlled process* | • functionality type (FTD)<br>• molecular architecture (MAD) | • irreversible adsorption<br>• determination of critical adsorption point |
| HPLC | • chemical composition<br>• endgroup<br><br>*adsorption controlled process* | • chemical composition (CCD)<br>• functionality type (FTD) | • molar mass influence<br>• partial adsorption<br>• large k' |

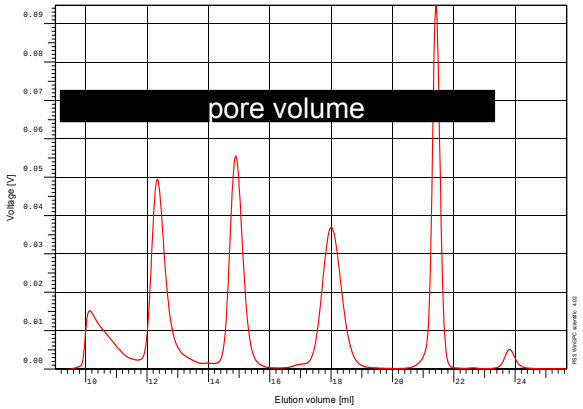


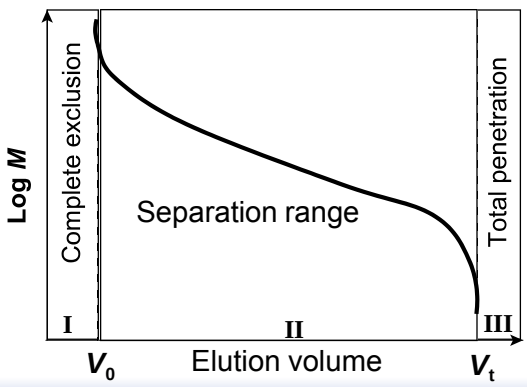
# Introduction

## SEC Separation Principles

- solutes diffuse between mobile phase and pores in stationary phase
- conformational entropy loss is driving force
- retention based on hydrodynamic size in solution $V_h$
- molar mass by rentention calibration or proper detection method





# Introduction

## SEC Instrumentation

Special instrumental requirements:
- solvent compatibility
- prevent clogging by solvent evaporation
- multi-detector application
- columns: mainly polymer packing
- often:
  - absolute concentrations required
  - absolute injection volume required

critical modules:
- pumps
- autosamplers
- software



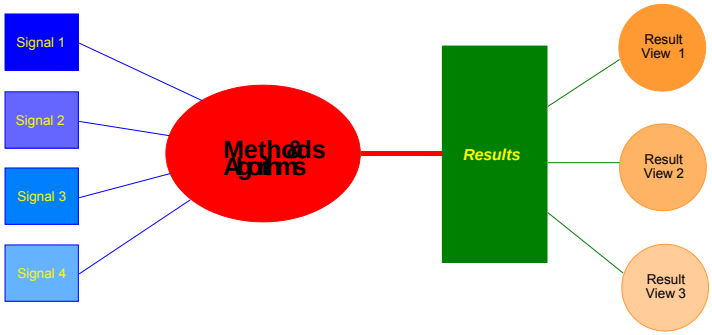

# Introduction

## SEC Data Systems

Special software requirements:

- long analysis times
- complex data treatment
- multi-signal processing
- determination of distributions
- combination of methods
- multiple vendor support
- integration in existing infrastructure

Plethora of Software Requirements

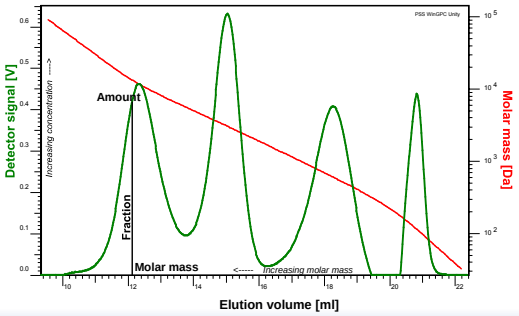
# Introduction

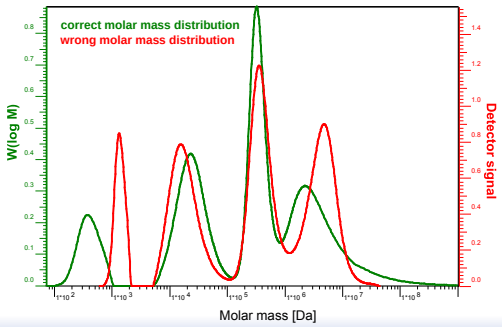
## Determination of Property Distributions

complete description of properties and contributions

- accurate determination of amounts
- proper measurement/calibration of properties
- accurate results calculation and representation

**Example**: Conversion of raw signals to molar mass distribution




The **molecular weight averages** can be calculated from the moments, $\mu_i$, of the molar mass distribution:

$$\mu_i = \int_0^\infty M^i \cdot w(M)\,\mathrm{d}M$$

with: $\mu_i$ the i-th moment of the molar mass distribution

**The molar mass averages are defined and calculated in PSS WinGPC Unity by:**

**Number average molecular weight**:

$$M_n = \frac{\sum h(M)\cdot M}{\sum h(M)} = \frac{\sum w(M)}{\sum w(M)/M} = \frac{\mu_0}{\mu_{-1}}$$

**Weight average molecular weight**:

$$M_w = \frac{\sum h(M)\cdot M^2}{\sum h(M)\cdot M} = \frac{\sum w(M)\cdot M}{\sum w(M)} = \frac{\mu_1}{\mu_0}$$

**z-average molecular weight**:

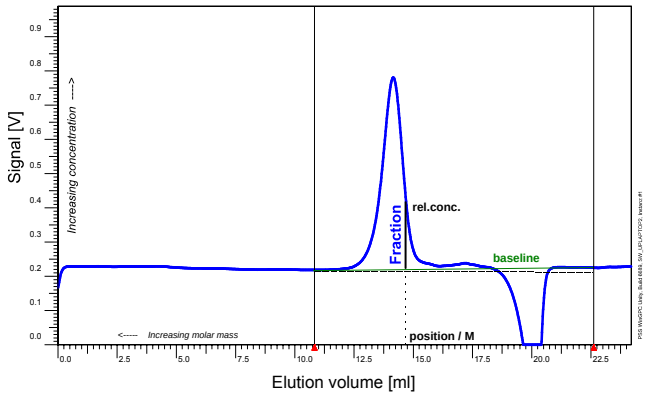
$$M_z = \frac{\sum h(M)\cdot M^3}{\sum h(M)\cdot M^2} = \frac{\sum w(M)\cdot M^2}{\sum w(M)\cdot M} = \frac{\mu_2}{\mu_1}$$

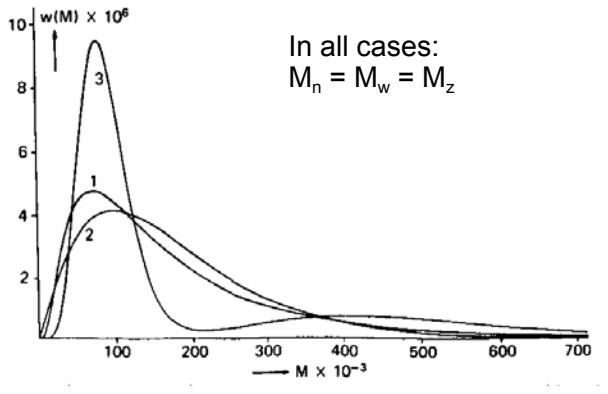


# Conventional Data Analysis

## Determination of fundamental parameters

| | |
|---|---|
| Chromatogram: | relates apparant concentration to elution volume / retention time |
| calibration curve: | relates molar mass to chromatographic position |
| molar mass distribution: | shows mass fraction of molecules of given molar mass |



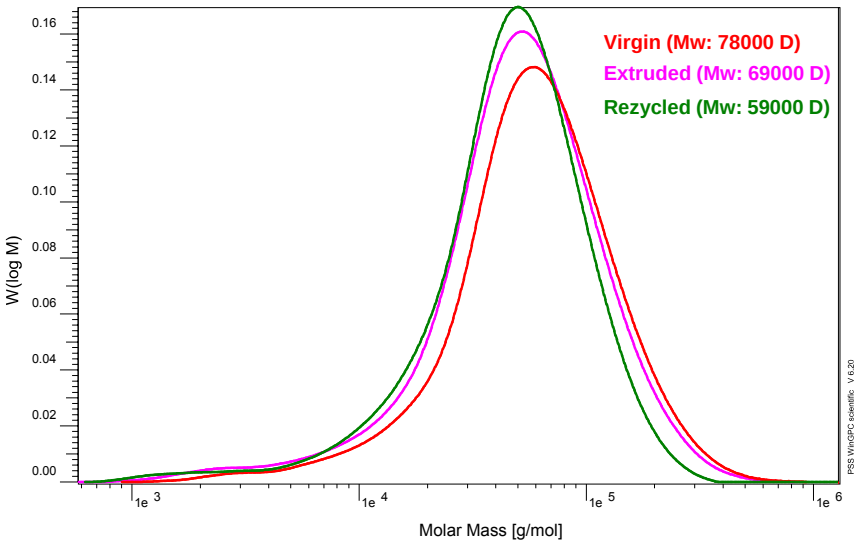

In all cases:
$M_n = M_w = M_z$

# Conventional Data Analysis

## Polymer Degradation during Recycling Processes

conditions:

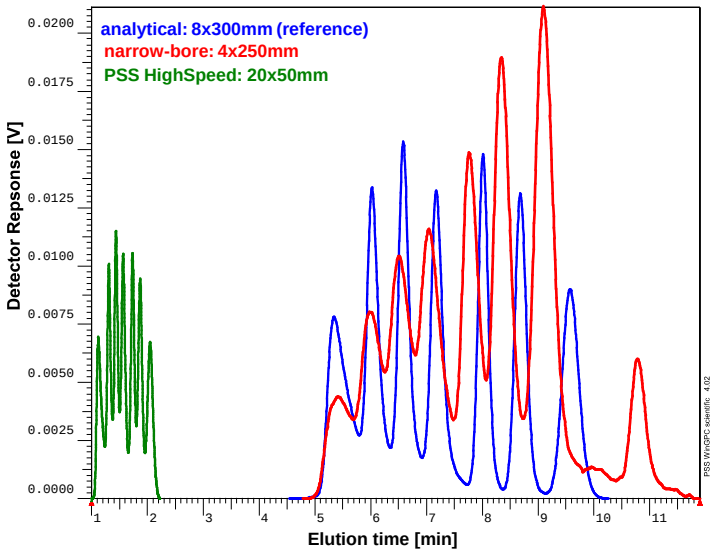
system: PSS SECcurity GPC
eluent: TCM/HFIP
columns: PSS SDV 5µm
detection: UV@260nm
software: PSS WinGPC
analysis in: 35 min / sample






# Conventional Data Analysis

## Conventional and HighSpeed Analysis

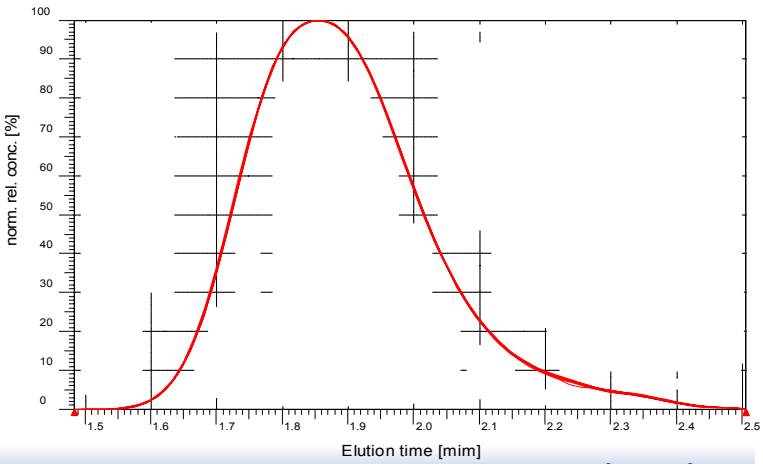


# Conventional Data Analysis

## Quality Assurance by HighSpeed SEC

Example: commercial polycarbonate in THF
mw by producer: 30000 g/mol
60 repeats in 2h

column: 2x PSS SDV 5 µm HighSpeed
calibration: PSS ReadyCal PS standards
detection: UV




HighSpeed result:

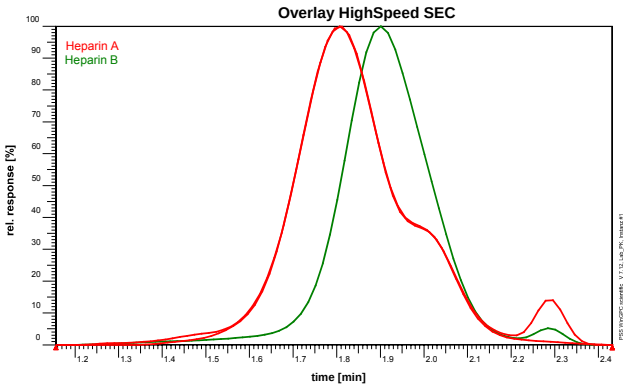
$M_w$: (29610±150) g/mol
RSD: 0.5%

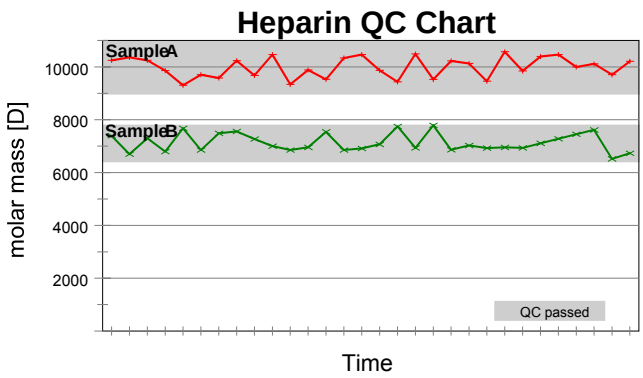


# Conventional Data Analysis

### HighSpeed Heparin Quality Assurance

column: PSS HighSpeed Suprema 100, 10 µm
analysis time: 2 min
calibration: Heparin endgroup (DAB); PSS WinGPC
detection: RI




- good Mw accuracy
- high reproducibility
- time savings: factor 10
- no change of instrumentation/method

# Chromatographic Modes of Separation

## Potential problems SEC

Separation range may be increased by using

longer or more columns

**Peak capacity:**

$$n = 1 + \frac{\sqrt{L}}{4} \cdot \ln \frac{V_p}{V_0}$$

**However:**
*n* independent properties require *n*-dimensional methods for accurate (independent) characterization.



# 2-Dimensional Chromatography

*n* independent properties require *n*-dimensional methods for accurate (independent) characterization.

Possible multidimensional chromatography techniques:

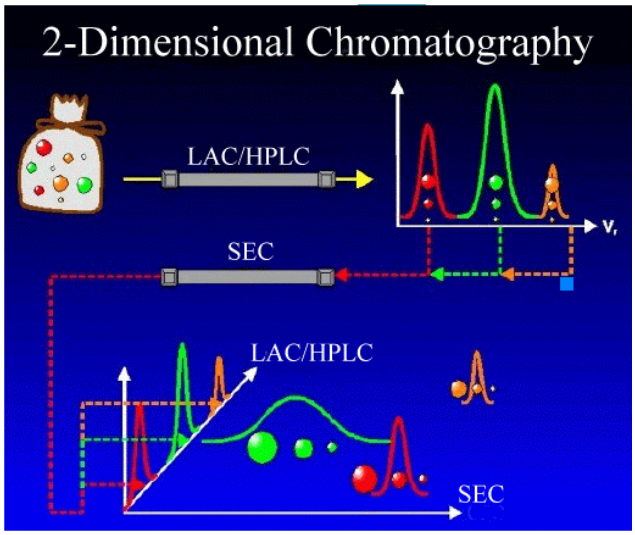
HPLC, SEC, LC-CC, GC, TREF, GPEC,.....

**Example:**

combination of LAC(HPLC) and SEC:

1st dimesion:
LAC/HPLC for separation according to CC

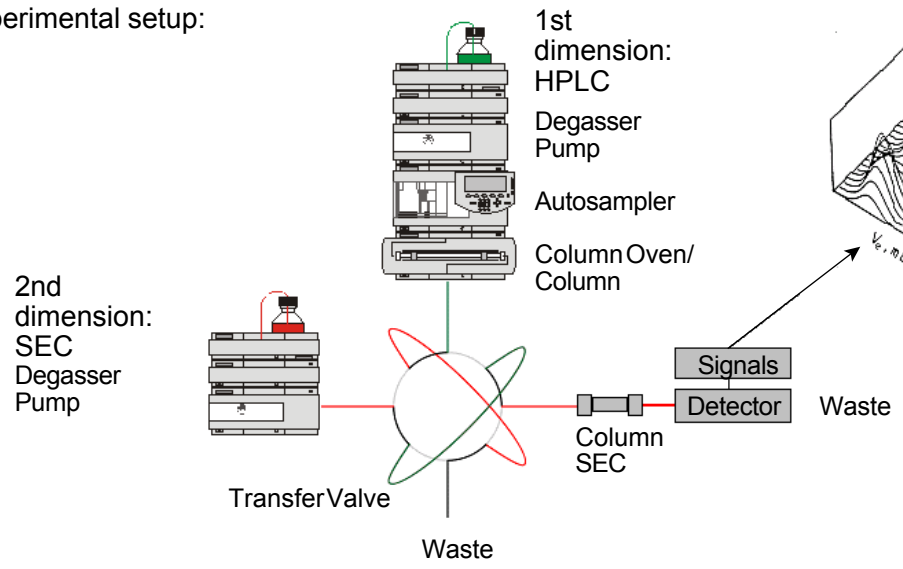
2nd dimesion:
SEC for separation according to MM



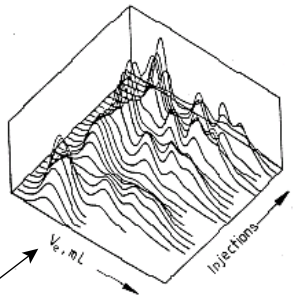
# 2-Dimensional Chromatography

## Investigation of CCD and MMD

Experimental setup:




SEC results (chromatograms)






# 2D Chromatography

## *GPC Analysis of TPE*

sample B failed in the field

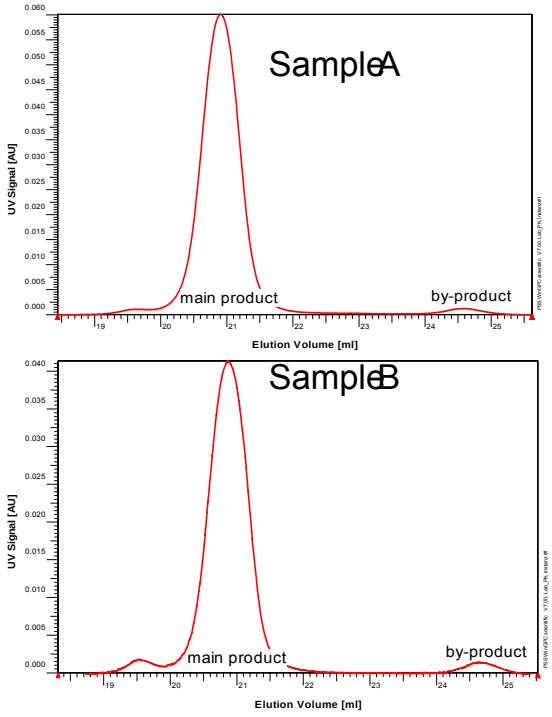
- main product looks very similar
- similar by-products present

GPC does not track performance differences

| | sample A | sample B |
|---|---|---|
| Mn[kD] | 99 | 90 |
| Mw[kD] | 109 | 103 |
| Mw/Mn | 1.08 | 1.14 |
| Mp[kD] | 108 | 104 |
| by-product | 0.8% | 1.7% |

molarmassesbynarrowPStcalibration

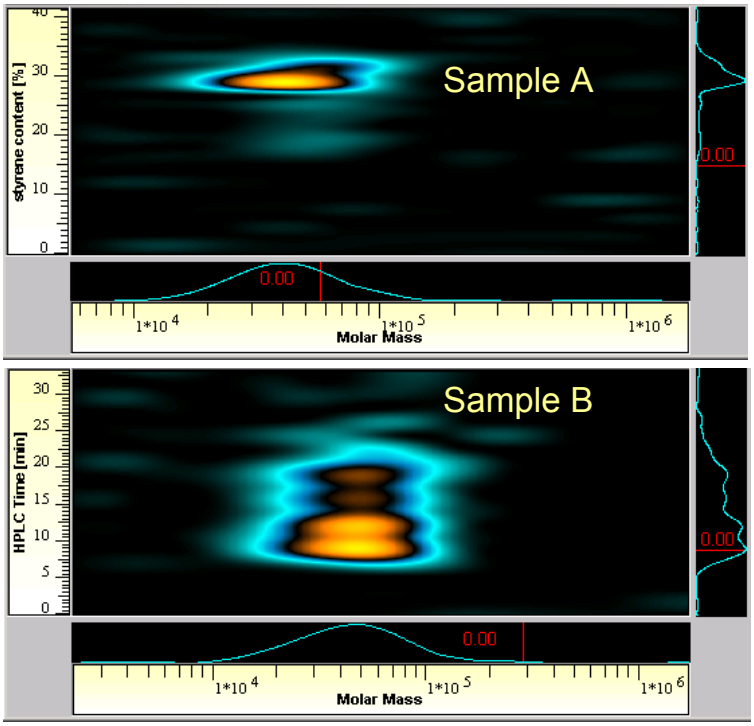
differencesduetocomposition?



# 2DChromatography

**Comprehensive 2D by HPLCxSEC**

HPLC tracking composition
SEC tracking molar mass




2D analysis

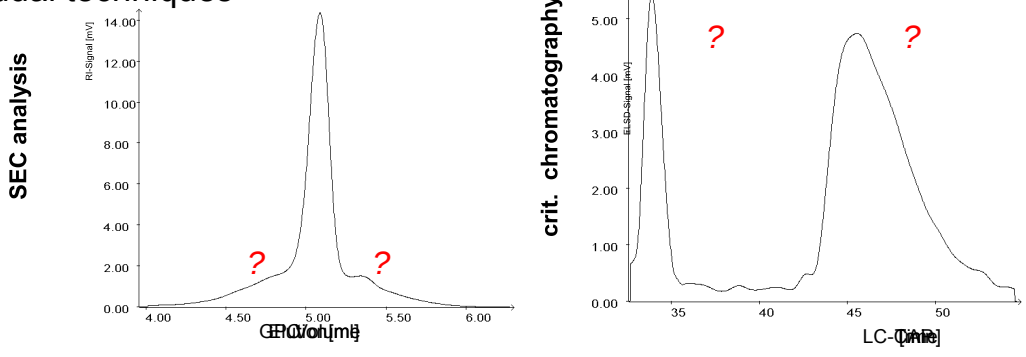
- corroborates similar MMD
- shows similar average PS content
- reveals big differences in CCD
- contour map shows
  - differences easily
  - 2D property distributions



# 2-Dimensional Chromatography

**Investigation of by-product in motor oil additives**

Individual techniques




observations difficult to explain

# 2-Dimensional Chromatography

## *Investigation of by-product in motor oil additives*

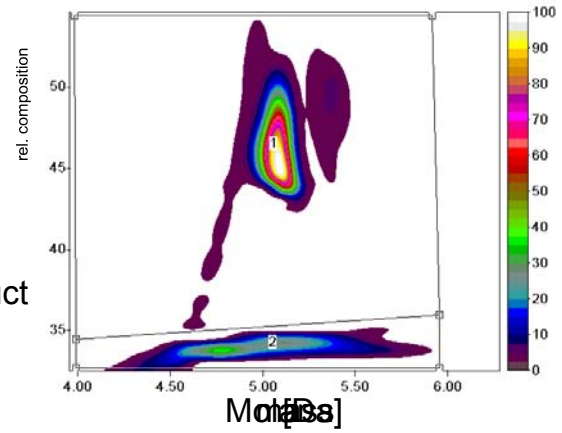
2Dcontourmap

**2D results**

-mainproduct(region1)
-parallelreactionformsregion2

-twodifferentprocesses
-by-productishomopolymer
-by-producthasbroadMMD

-reactionmixturecontains60%desiredproduct
-desiredproductisnarrowinCCDandMMD





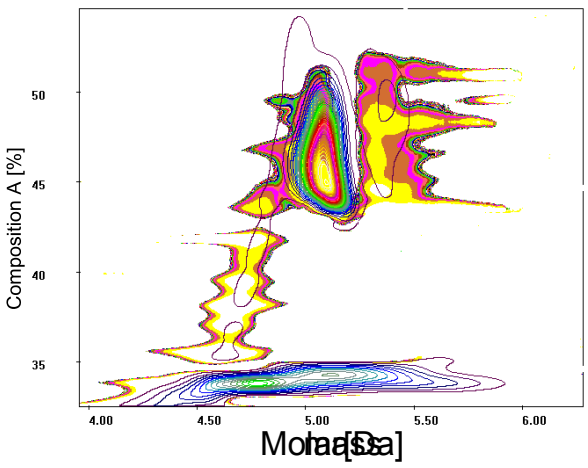

# 2-Dimensional Chromatography

## *Investigation of by-product in motor oil additives*

**2Dcompositionalanalysis**

overlayof2Dseparation
withchemicalcomposition

supports
-twosimultaneouspolymerizationprocesses
-desiredproductiscopolymer
-by-productishomopolymer




SEC Workshop: PolyChar 18, Siegen 2010 www.polymer.de

# Multi-Dimensional Chromatography

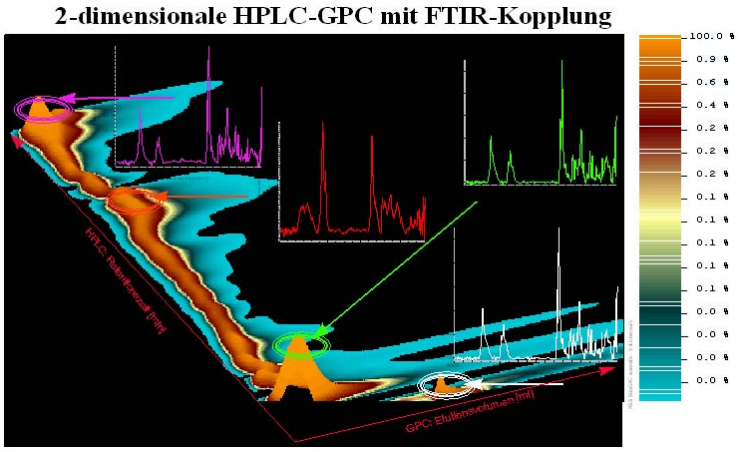
***Investigation of complex plant extracts***

Sample mapping

sample
-chemically complex
-polydisperse in molecular size

high peak capacity due to:

$$n_{2D} = n_1 \cdot n_2$$




online identification by FTIR library search



# 2-Dimensional Chromatography

## Practical advice

**Selection of Separation Techniques:**
CE, GC, SFC, TREF, FFF
Destructive methods (GC and SFC) can only be used in the final separation dimension.

**Sequence of Separation Methods:**
Method with the highest selectivity (for one property) as the first dimension.

**Eluent Transfer:**
Complete miscibility of the mobile phases is required.

**Time Consumption:**
1 HPLC run, many SEC runs (time consuming):
with HighSpeed SEC analysis time can be significantly reduced.

**Detectability and Sensitivity in the Second Dimension:**
Detectors with high sensitivity for detecting the diluted fraction:
ELSD (evapurating light scattering detector) or UV/VIS

# Detection Techniques in SEC

## Useful Methodologies

for MMD: conventional SEC with concentration detection and matching polymer standard

for CCD: conventional SEC utilizing multiple concentration detection

for MMD, FTD: on-line analysis of SEC fractions with a mass spectrometer (ESI, MALDI)

for MMD, MAD: on-line analysis of SEC fractions with a LS detector and/or viscometer

for CCD, MMD: simultaneous separation and identification by LC-FTIR and NMR detection

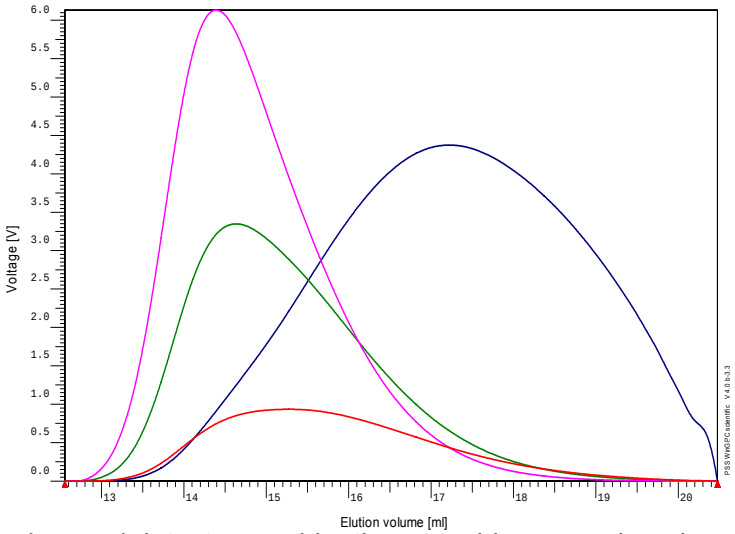
for CCD, MMD, MAD, FTD:
comprehensive 2D chromatography with multiple detection



# Detection Techniques in SEC

## Detector Properties

Detector Signal Characteristics




*x=0 : concentration detector*
Refractive index detector (RI)

*x≠0 : molar mass sensitive detectors*
On-line light scattering detector

On-line viscosimeter

On-line NMR

advanced detector combinations provide comprehensive molecular and structural information

# Detection Techniques in SEC

## Detector Signal Characteristics

$$U_d = K_d \times \sum_i \left( k_{Sample} \times c_{Sample} \times M^x \right)$$

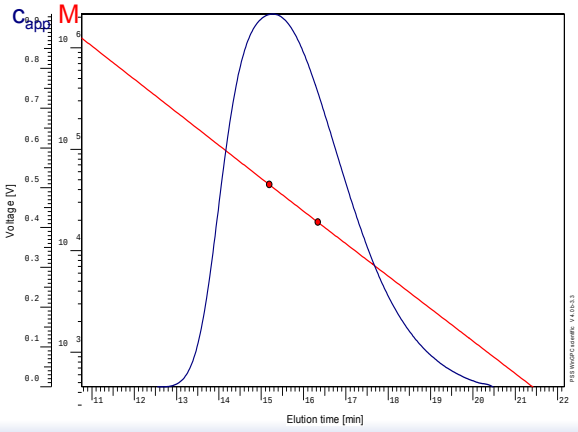
| | | |
|---|---|---|
| $U_d$: | Signal intensity | |
| $K_d$: | Instrument constant | |
| $k_{sample}$: | Sample dependent parameter | |
| | for spectroscopic detectors: | $k_{sample}$ = extinction coefficient, κ |
| | for refractive index (RI) detectors: | $k_{sample}$ = refractive index increment, dn/dc<br>note: dependent on solvent composition, T, λ |
| $c_{sample}$: | Sample concentration | |
| M: | Molar mass | |
| x: | Detector dependent | |
| | for RI, UV, ELSD: | X = 0 |
| | for on-line LS and MS detectors: | X = 1 |
| | for on-line viscometers: | X = Mark Houwink coefficient α |
| | for on-line NMR, osmometers* : | X = -1 |
| | | * not commercially available |



# Determination of Chemical Heterogeneity

## Multiple Detection in SEC Mode

What we need: c(V), $M_c$(V) ➔ $x_k$(M), w(log $M_c$), $M_{n,c}$, $M_{w,c}$, $D_c$
What we have: $c_{app}$(V), M(V)




*advantages:*
- uses ordinary SEC equipment
- copolymer analysis with same injection
- no additional sample preparation

*limitations:*
- statistical copolymers
- graft copolymers with high graft density

# Determination of Chemical Heterogeneity

## MultipleDetectioninSECMode

*Approach:*

Task1: derivetruec(V)from$c_{app}$(V)
needsmulti-detectorsetupwithdetectorcalibration

$$\begin{pmatrix} U_1 \\ . \\ . \\ U_i \end{pmatrix} = \begin{pmatrix} f_{11}w_1 & .. & .. & .. \\ .. & .. & .. & .. \\ .. & .. & .. & .. \\ .. & .. & .. & f_{ik}w_k \end{pmatrix} \cdot c_{true}$$

$U_i$ responseindetector*i*
$f_{ik}$ responsefactorforcomponent*k* in detector*i*
$w_k$ weightfractionofcomponent*k*
$c_{true}$ concentrationofsample

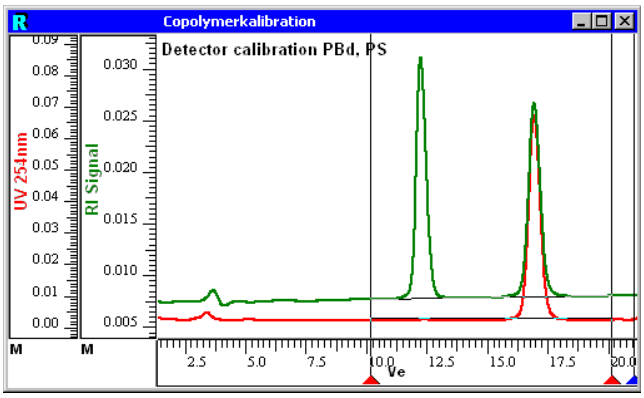
➜absoluteconcentrationofallcomponents*k*insample

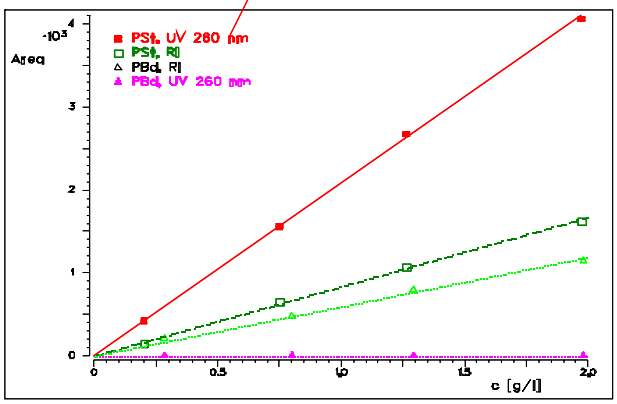


# Determination of Chemical Heterogeneity

## MultipleDetectioninSECMode

Determinationofcopolymerresponsefactors



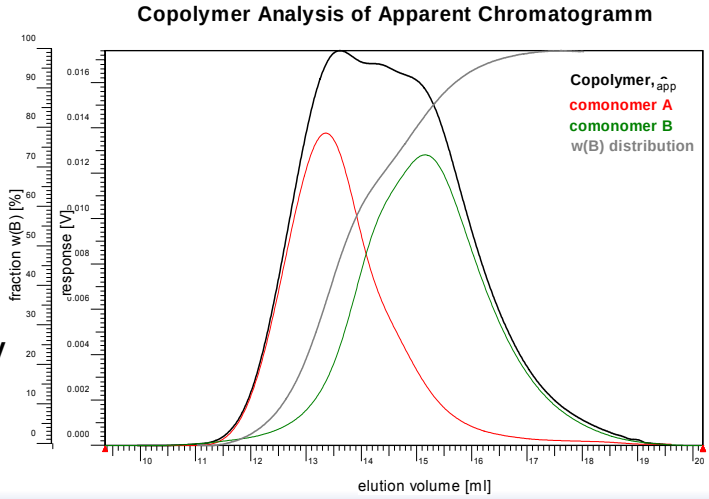



# Determination of Chemical Heterogeneity

## Multiple Detection in SEC Mode

Determination of comonomer concentrations

$$c_{app} = \sum_k f_{dk} \cdot c_k$$




*advantages:*
- universal approach
- no special equipment necessary

*limitation:*
- neighbor-group effects

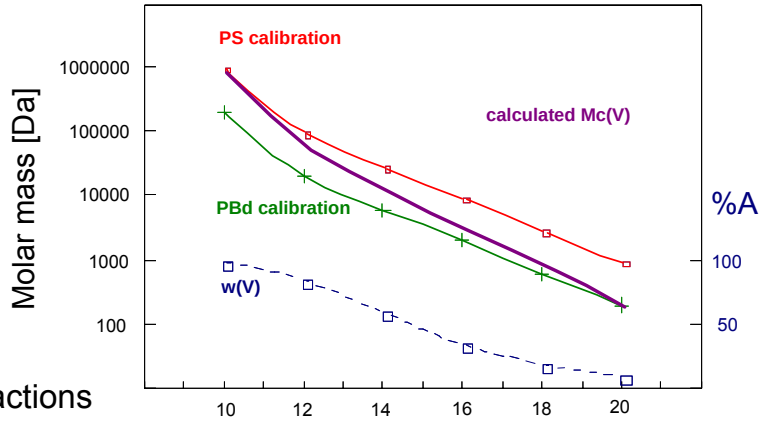


# Determination of Chemical Heterogeneity

## Multiple Detection in SEC Mode

Task 2: $M_c(V)$ from homo polymer calibration, or
$M_c(V)$ directly from molar mass sensitive detection

$$\lg M_c(V) = \Sigma\, w_k(V) \cdot M_k(V)$$




correct for negligible hetero-contact interactions

# Determination of Chemical Heterogeneity

***Investigation of ABA block copolymer in SEC Mode***

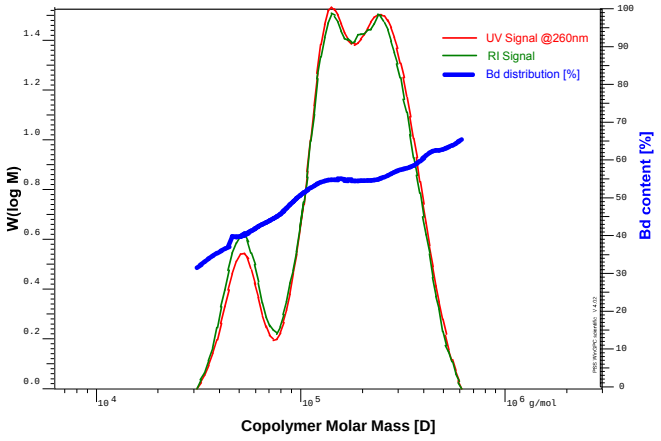
GPC results with PS standards:

Mn 127kDa
Mw 353kDa
PD 2.78

Copolymer results with multidetection:

Mn 76.3kDa
Mw 222kDa
PD 2.91

by PS and PBd calibration






# Determination of Chemical Heterogeneity

**Separation in LAC Mode**

Separation of species according to interactivity

composition average:

$$\bar{G} = \mu_1(G) = \frac{\sum c_i \cdot G_i}{\sum c_i}$$

width of distribution:

$$dG = \sqrt{\mu_2(G) - (\mu_1(G))^2} = \sqrt{\frac{\sum c_i (G_i - \bar{G})}{\sum c_i}}$$

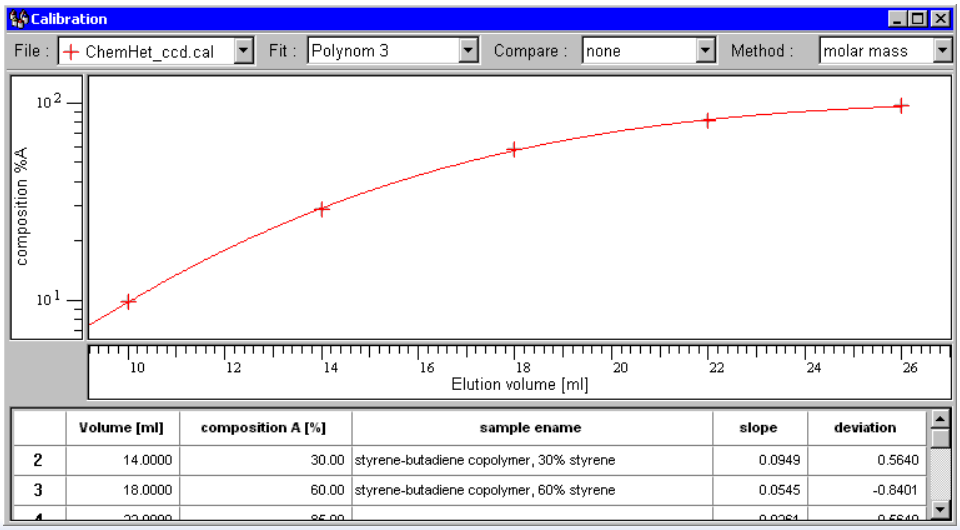
skew of distribution:

$$S = \frac{\frac{\sum c_i (G_i - \bar{G})^3}{\sum c_i}}{2\left(\frac{\sum c_i (G_i - \bar{G})^2}{\sum c_i}\right)^{3/2}}$$

# Determination of Chemical Heterogeneity

## SeparationinLACMode

Retentiocalibration:




| | Volume [ml] | composition A [%] | sample ename | slope | deviation |
|---|---|---|---|---|---|
| 2 | 14.0000 | 30.00 | styrene-butadiene copolymer, 30% styrene | 0.0949 | 0.5640 |
| 3 | 18.0000 | 60.00 | styrene-butadiene copolymer, 60% styrene | 0.0545 | -0.8401 |



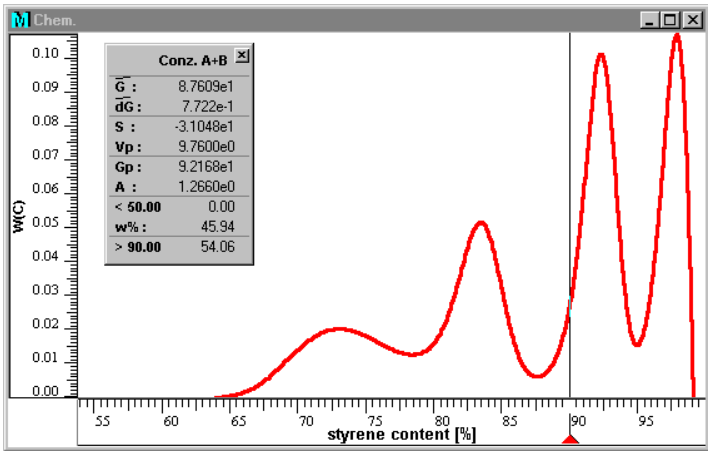
# Determination of Chemical Heterogeneity

## SeparationinLACMode

***Mixture of styrene-butadiene copolymers***

-goodseparation
-extensivequatification
-comprehensive heterogeneityinformation
-determinationof high/lowfractions

veryusefulforstatistical copolymers

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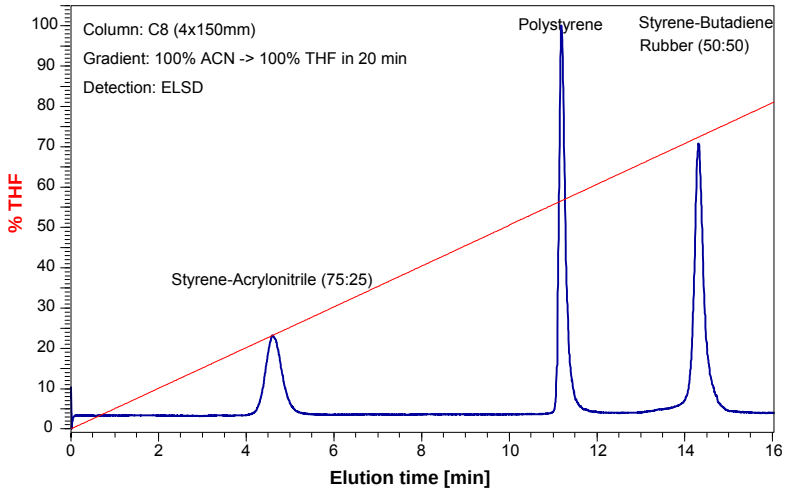
# Determination of Chemical Heterogeneity

## SeparationinLACMode

***mixture of styrene copolymers***

-highselectivityofphase system
-wellresolvedaccording to sample polarity



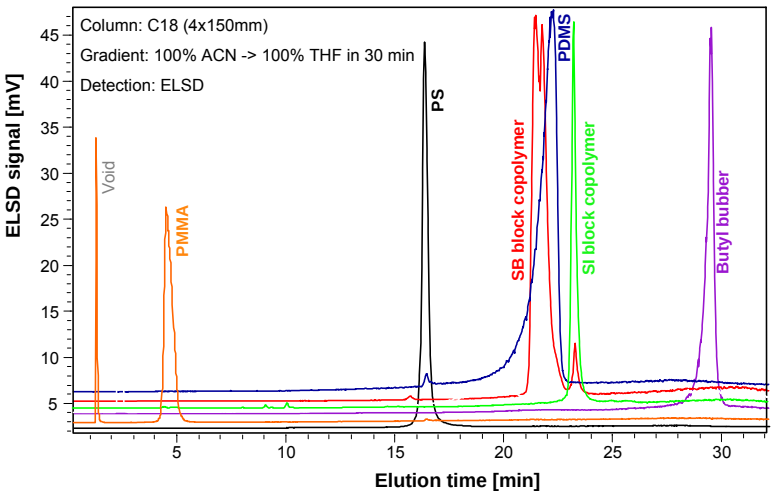



# Determination of Chemical Heterogeneity

## SeparationinLACMode

***mixture of different polymers***

-interactionveryselective
-separationbasedon sample polarity
-simplegradient
-detectionneedsELSD (quantificationproblem)



# Detection Techniques in SEC

## SEC with multiple concentration detection — CCD information

$$U_D = K_D \times \sum_i (k_{Sample} \times c_{Sample})$$

For two components:

$$U_D = K_D \times (k_{Sample1} \times c_{Sample1} + k_{Sample2} \times c_{Sample2}) = k'_{Sample1} \times c_{Sample1} + k'_{Sample2} \times c_{Sample2}$$

and 2 detectors, RI and UV:

$$U_{RI} = k^{RI}_{Sample1} \times c_{Sample1} + k^{RI}_{Sample2} \times c_{Sample2} \qquad U_{UV} = k^{UV}_{Sample1} \times c_{Sample1} + k^{UV}_{Sample2} \times c_{Sample2}$$

Homopoylmers can be used to measure k' for each detector. This allows quantification and molar mass determination.

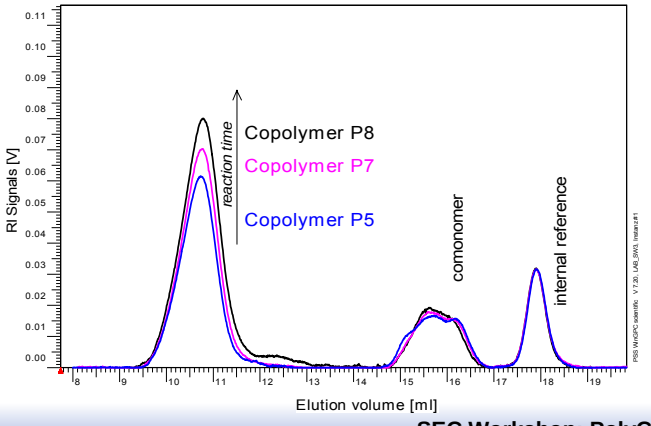


# Detection Techniques in SEC

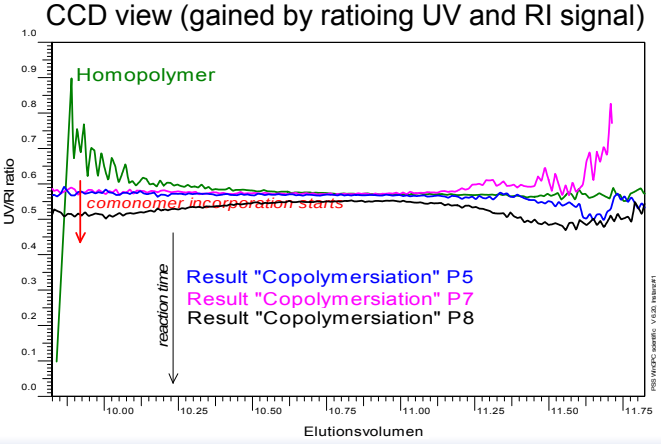
## SEC with multiple concentration detection — CCD information

**Example 1, qualitative:** block-copolymers from a kinetic run,
2 different monomers were used,
samples were drawn after different reaction times (P1-P8)

raw data view (overlay, only RI signal shown)




CCD view (gained by ratioing UV and RI signal)

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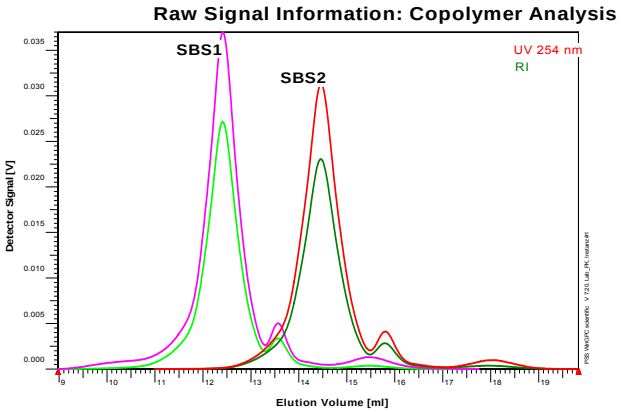
# Detection Techniques in SEC

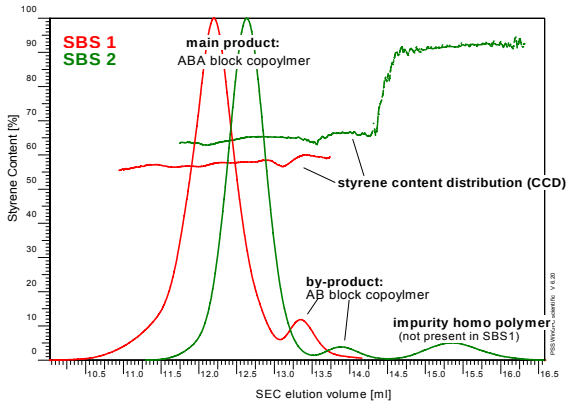
## SEC with multiple concentration detection: CCD information

**Example 2, quantitative analysis**

raw data view (overlay)




CCD view




MMD of copolymer can be measured by establishing a copolymer calibration curve

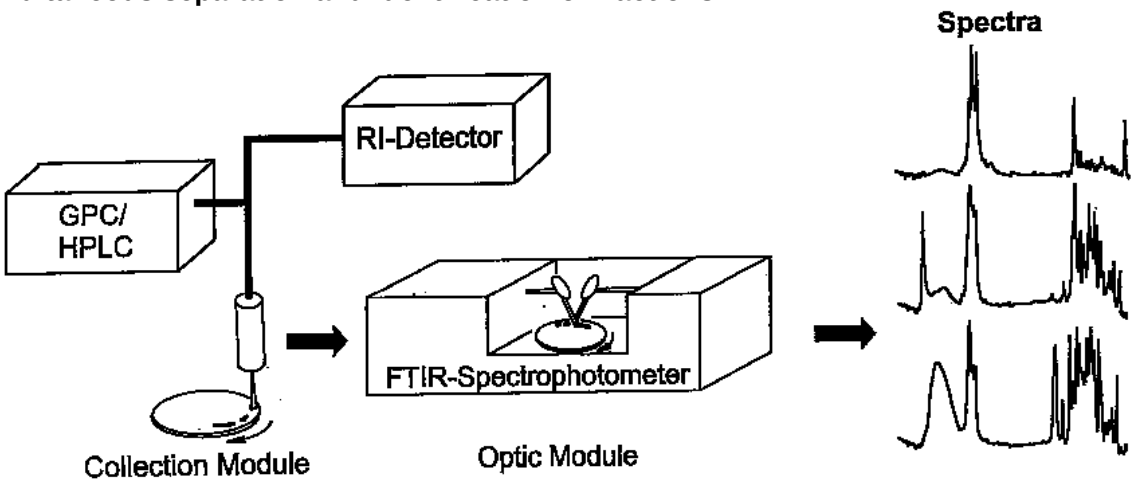
**Requirements**: CCD, calibration curve PS, calibration curve PBd



# Detection Techniques in SEC

## SEC with FTIR detection: CCD, MMD information

**Simultaneous separation and identification of fractions**



# Detection Techniques in SEC

## SEC with FTIR detection: CCD, MMD information

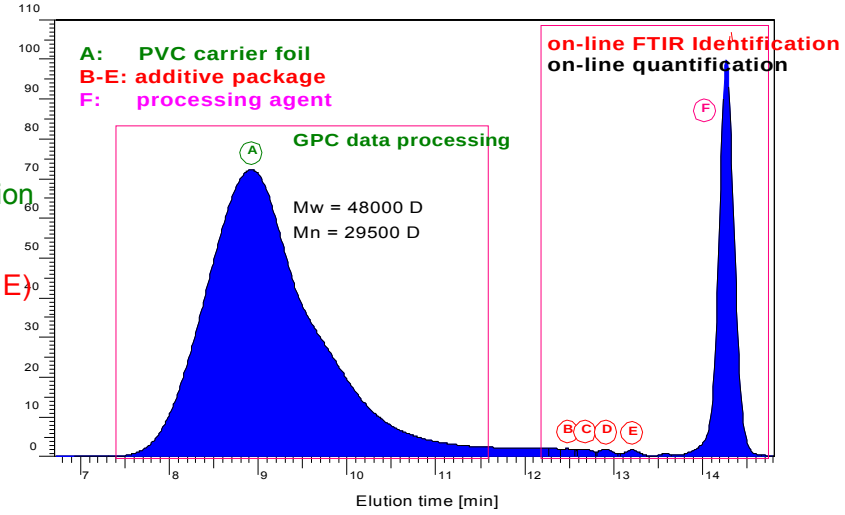
type and nature of the polymer used (peak A: PVC)

molar masses and molar mass distribution of the polymer (peak A)

identification of the additives (peaks B - E)

quantification of all additives in the packaging foil

identification and quantification of the processing agent (peak F)






# SEC with MS Detection

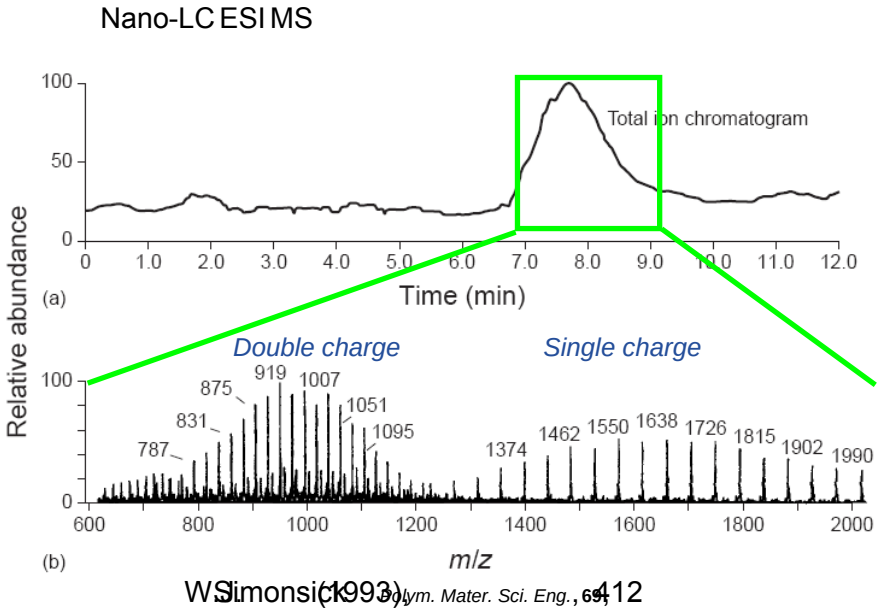
## Basics

**MSadvantages:**

- absolute molar mass
- repeat unit identification
- endgroup determination
- structure elucidation

**disadvantages:**

- hmw limitations
- discrimination (MALDI)
- multiple charges (ESI)
- copolymers difficult




W. Simonsick (1993) *Polym. Mater. Sci. Eng.*, 69, 412

# SEC with MS Detection

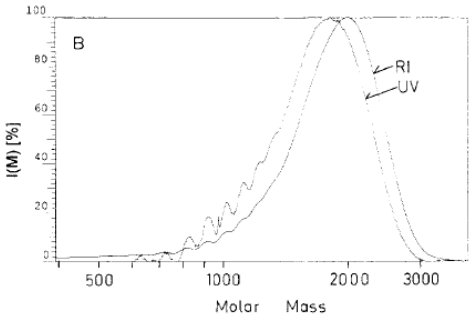
## Basics

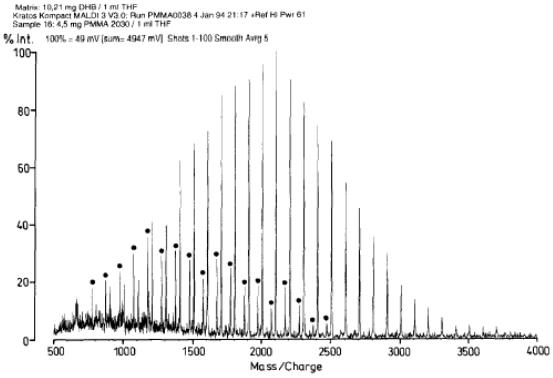
**MALDIadvantages:**

- absolute molar mass
- repeat unit identification
- endgroup determination
- structure elucidation
- high molar mass range

**disadvantages:**

- matrix influnces
- discrimination in polydisperse samples
- only offline mode (spotting)
- copolymers difficult




GPC-MALDI of PMMA
Ref.: Gores, Pasch; *Polymer* **36**, 1999

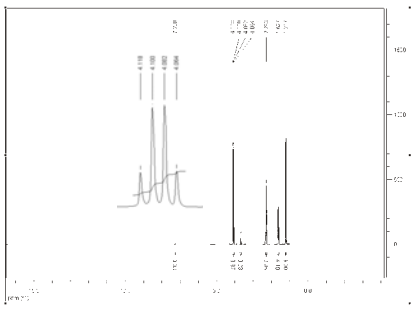
Figure 4 M.a.l.d.i.-m.s. spectrum of a PMMA calibration standard (sample 3); full circles indicate the cyclic oligomers



# SEC with NMR Detection

## Basics

NMR can be used as a (universal) chemical detector
NMR is a chemical sensor looking at local chemical environment
ideal for structure elucidation: chemical shift, J coupling



**High-field NMR couling**

non-destructive
super-conductivemagnet
highresolution
small differences obvious
expensive
complex
large
time-consuming
interfacing difficult
high operational cost
expert knowledge required


**Low-field NMR detection**

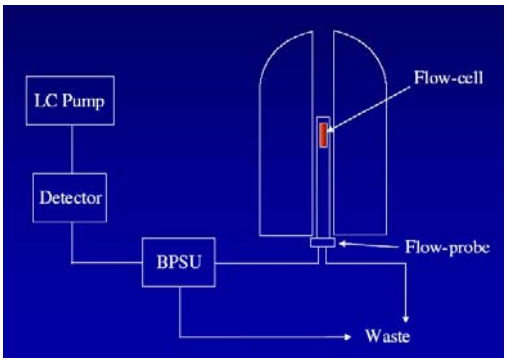
non-destructive
permanentmagnet
lowresolution
major sample characteristics
inexpensive
simple to use (detector)
smallbenchtop
low operation cost
flexible
modularsetups
saves sample prep time

# SEC with NMR Detection

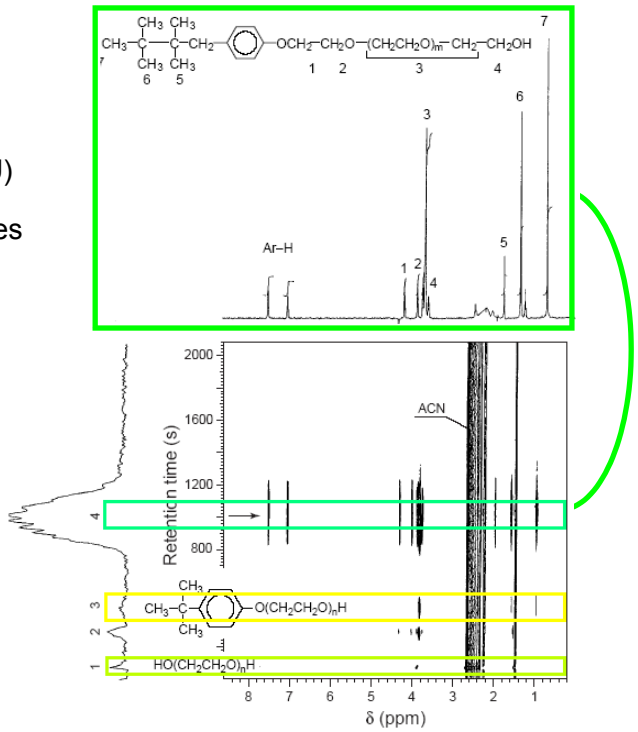
## High-Field NMR Coupling to HPLC

Sample: non-ionic surfacrants

- samples have been stored in storage valve (BPSU)
  Offline NMR scans
- solvent signals eliminated by NMR pulse sequences




Ref.: Pasch/Hiller (1996), Macromolecules, 2, 6556





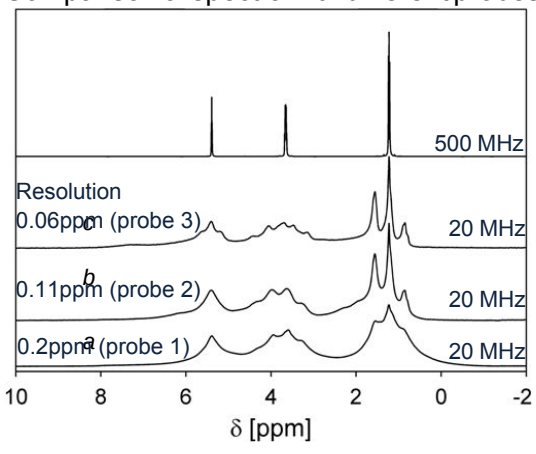

# SEC with NMR Detection

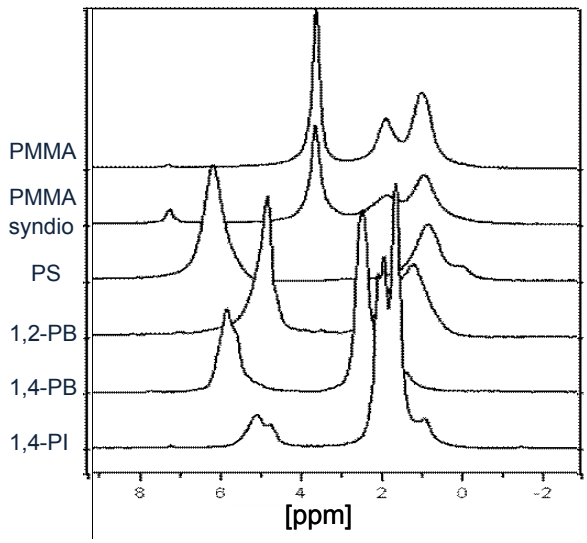
## Current Status

base NMR: Bruker TopSpin, 20 MHz magnet
automatic supression of solvent peaks
0.2ml probe
scan time: 2 secs

run on: PSS SECcurity GPC system, single PSS SDV 5µm column, THF
typical SEC injection conditions

Comparison of spectra with different probes



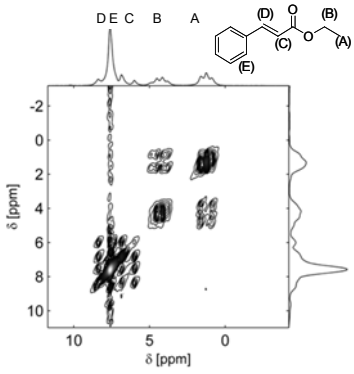



# SEC with NMR Detection

## CurrentDevelopments

- 60MHz permanent magnet
- probe optimization
- PSS WinGPC software solutions
- investigation of limitations (2D NMR)

2D-COSY spectrum
Cinnamic Acid Ethylester
measuring time: 8h
connectivities visible




**Intended Use**

- Teaching and training for high-end NMR, or nano-money NMR (nm-NMR)
- Fast, quantitative analysis for known systems (food, wine, ...) high throughput via flow probe
- "In-lab NMR" for fast batch chemical detection and quantification
- at-site NMR, close to reactor, moveable, flow probe, sensitivity 0,2 %
- low-field GPC-NMR for synthetic or bio-polymers
- low-field GPC-NMR: quantitative and chemical selective
- low-field GPC-NMR currently under development at PSS, Bruker & KIT



# Detection Techniques in SEC

## SEC with a light scattering detector: MMD, MAD information

**Theoretical Background Light Scattering:**

for monodisperse samples, diluted solutions, particle size < $\lambda/20$

$$R(\theta) = K \cdot c \cdot M$$

K: Optical constant, includes refractive index increment $(dn/dc)^2$
M: Molar Mass
c: Concentration

for polydisperse samples with larger partical size (non-isotropic scatterer):

$$K \cdot c/R(\theta) = 1/M_w \, [1+16/3 \, \pi^2/\lambda^2 \, \langle R^2 \rangle_z \, \sin^2(\theta/2)] + 2 \, A_2 \cdot c$$

# Detection Techniques in SEC

## SEC with a light scattering detector: MMC, MAD information

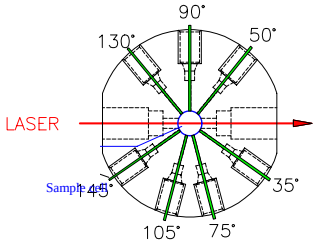
**Theoretical Background Light Scattering:**

$$K \cdot c / R(\theta) = 1/M_w \, [1 + 16/3 \, \pi^2/\lambda^2 \, \langle R^2 \rangle_z \sin^2(\theta/2)] + 2 \, A_2 \cdot c$$

Light scattering techniques:

LALLS: Low angle laser light scattering
RALLS: Right angle laser light scattering
MALLS: Multi angle laser light scattering

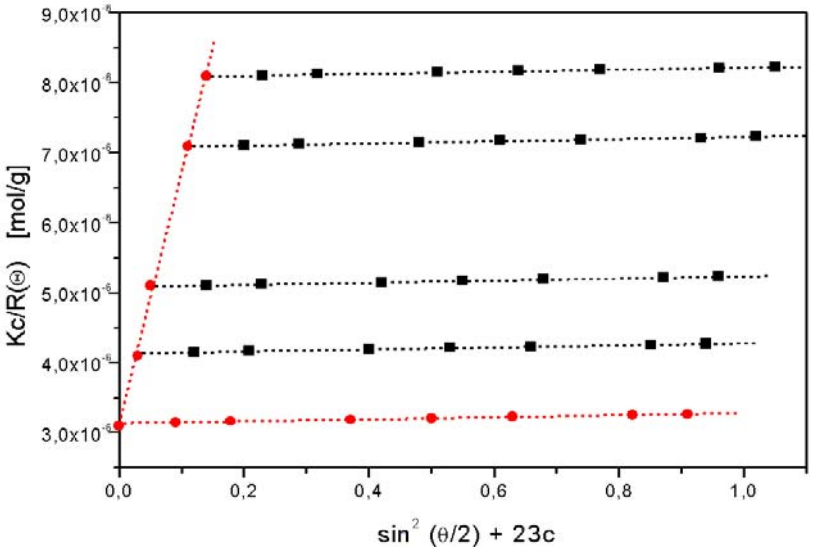
MALLS: Example for detector cell






# Detection Techniques in SEC

**Theoretical Background Light Scattering:**




**Zimm Plot:**

7 scattering angles: 35° to 145°
4 concentrations

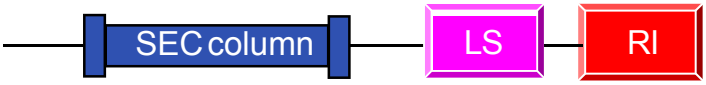
**Results:**

Intercept: $1/M_w$
Slope angular dependence: $\langle R^2 \rangle_z$
Slope concentration dep. : $A_2$

All bulk properties, no distribution information!

# Detection Techniques in SEC

## SEC with a light scattering detector: MMD, MAD information

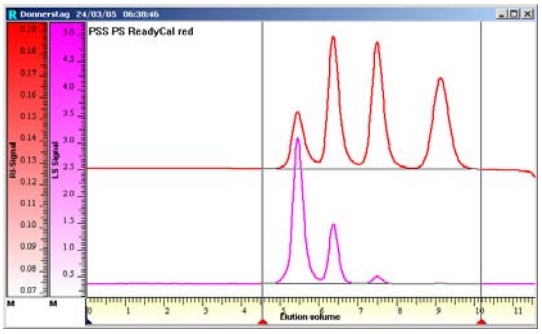



LS can be MALLS, RALLS, LALLS

LS signal: $U(LS) = K' \cdot (dn/dc)^2 \cdot c \cdot M$

RI singal: $U(RI) = K'' \cdot c$

$$\frac{LS - Signal}{RI - Signal} \rightarrow M \cdot (dn/dc)^2$$




| | | | | |
|---|---|---|---|---|
| Molar Mass | 1.090.000 | 130.000 | 17.800 | 1.620 D |
| Concentration | 0.6334 | 1.2669 | 1.2669 | 1.2669 mg/ml |

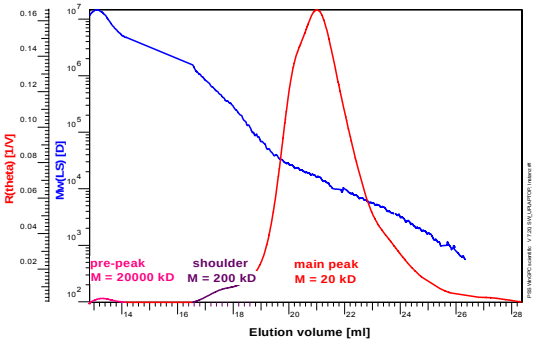


# Detection Techniques in SEC

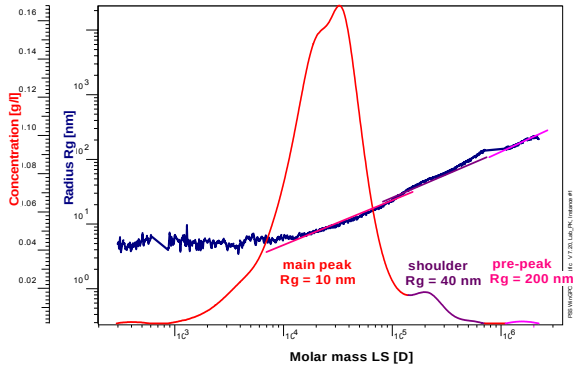
## SEC with a light scattering detector: MMD, MAD information

PVB (Poly-vinyl butyral) sample: SEC-MALLS

Results on-line Zimm plot:




molar mass measured for every fraction
MMD




radius of gyration measured for every fraction
MAD

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# Detection Techniques in SEC

## SEC with a viscometer detector: MMD, MAD information

**Theoretical Background:**

SEC separates according to hydrodynamic volume

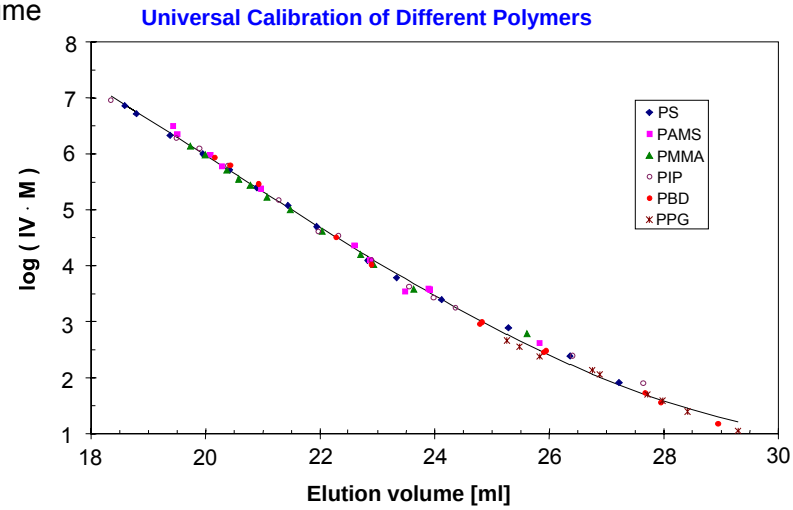
$V_{h,1} = V_{h,2}$

$[\eta]_1 \cdot M_1 = [\eta]_2 \cdot M_2$

A chance to solve the calibration dilemma:
Universal calibration curve

$M_2 = [\eta]_1 \cdot M_1 / [\eta]_2$

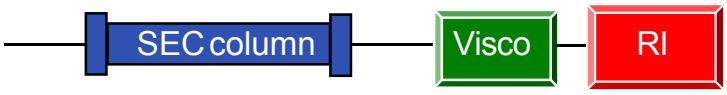
$[\eta]_2 = K \cdot M_2^{\alpha}$ Mark-Houwink equation
Structure information






# Detection Techniques in SEC

## SEC with a viscometer detector: MMD, MAD information

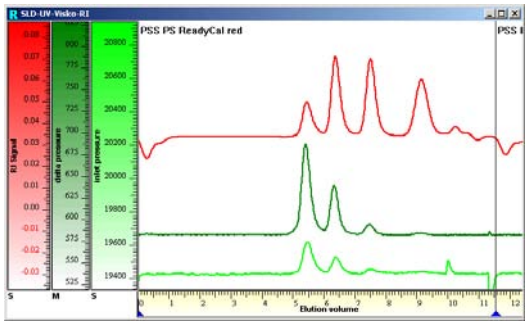



Viscometer signal: $U(V) = K' \cdot [\eta] \cdot c$

RI signal: $U(RI) = K'' \cdot c$

$$\frac{Visco - Signal}{RI - Signal} \rightarrow [\eta]_{Sample} \rightarrow$$ M from universal calibration curve

MMD



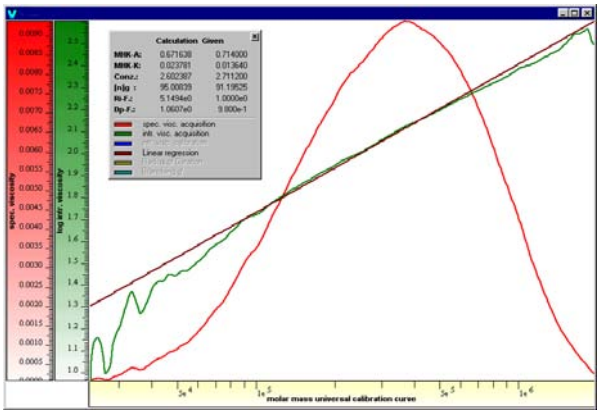
# Detection Techniques in SEC

## SEC with a viscometer detector: MMD, MAD information

Structure information, MAD:

$[\eta] = K \cdot M^{\alpha}$ Mark-Houwink equation

| | |
|---|---|
| $\alpha = 2$ | rigid rod |
| $1 > \alpha > 0{,}5$ | random coil |
| $\alpha = 0{,}5$ | random coil,Theta-conditions |
| $\alpha = 0$ | solid sphere |



Branching coefficient g': $g' = \{[\eta]_{branched}/[\eta]_{linear}\}_M$



# Conclusions

- comprehensive SEC/GPC is an established and versatile method
- plethora of LC and detection methods for structure investigation
- information request determines chromatographic strategy
- in-depth characterization of MMD, CCD, FTD, MAD, etc possible
- combination of LC modes opens new horizons
- increase of peak capacity by 2D chromatography
- unbiased investigation of property distributions
- mapping of samples or property quantification in 2D
- information-rich detectors add identification to separation