Sveučilište u Zagrebu
Fakultet kemijskog
inženjerstva i tehnologije

University of Zagreb
Faculty of Chemical Engineering and Technology

Structure and properties of polymer materials

seminars

Zagreb, October 2021

Determination of molecular weight of polymers

Molecular weight
Key characteristics of the polymers determining its properties

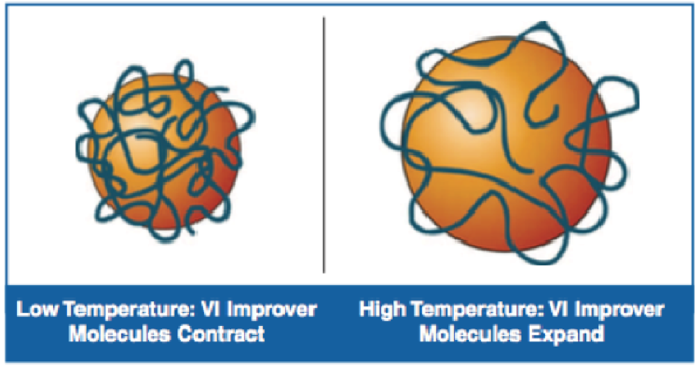
Some natural polymers – uniquely defined molecular weight
All synthetic and some natural polymers:

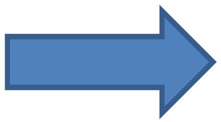
- Non-uniformity
- Dispersity
- Molecular weight distribution:

is it better to have a wide or a narrow distribution?

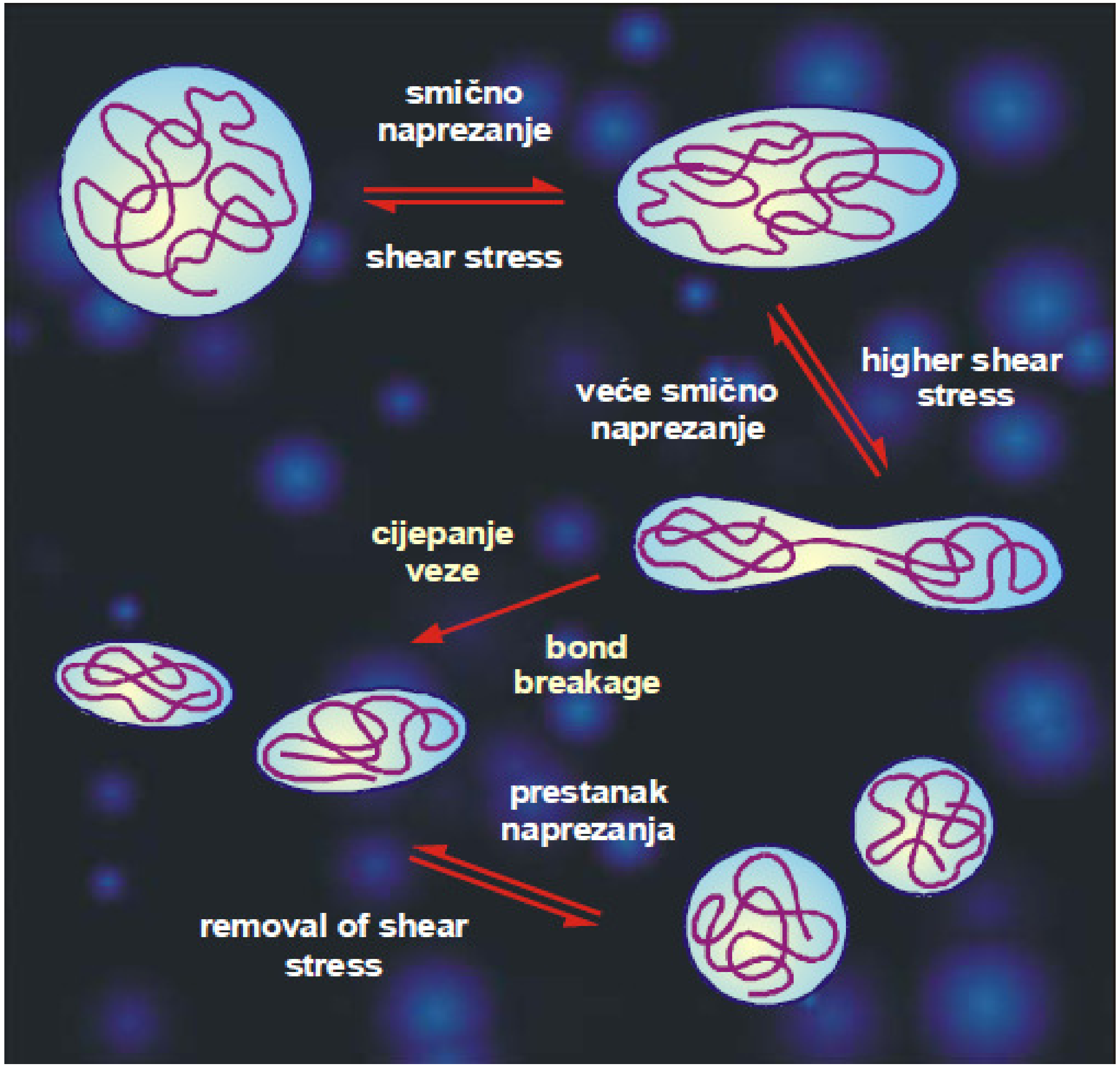
Examples:

- Processability – melt viscosity
- Penetration through membranes
- Polymers as additives for motor lubricants





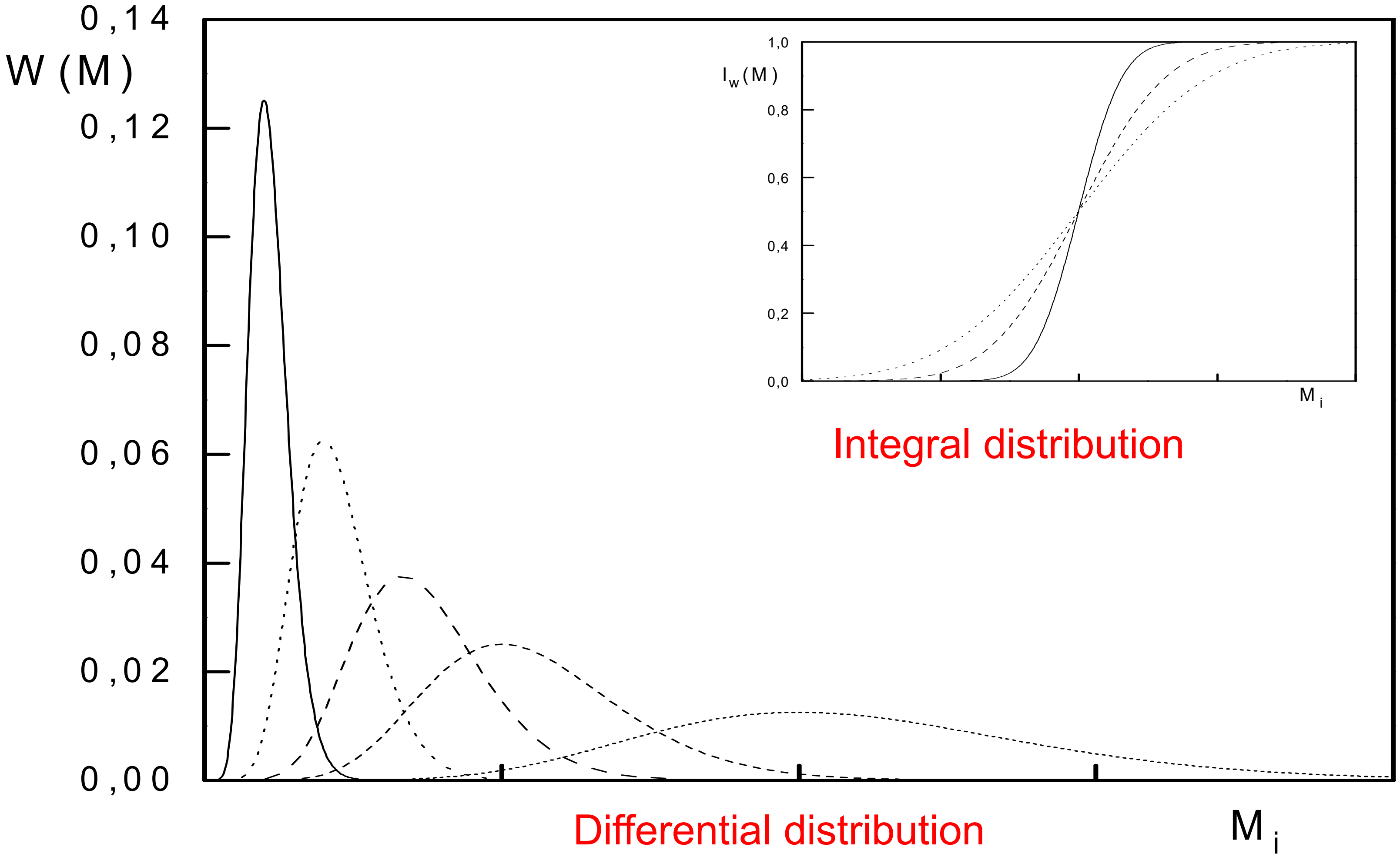
Too large molecules break under applied shear stress


smično
naprezanje
shear stress
veće smično
naprezanje
higher shear
stress
cijepanje
veze
bond
breakage
prestanak
naprezanja
removal of shear
stress

Determination of molecular weight of polymers

Molecular weight distributions

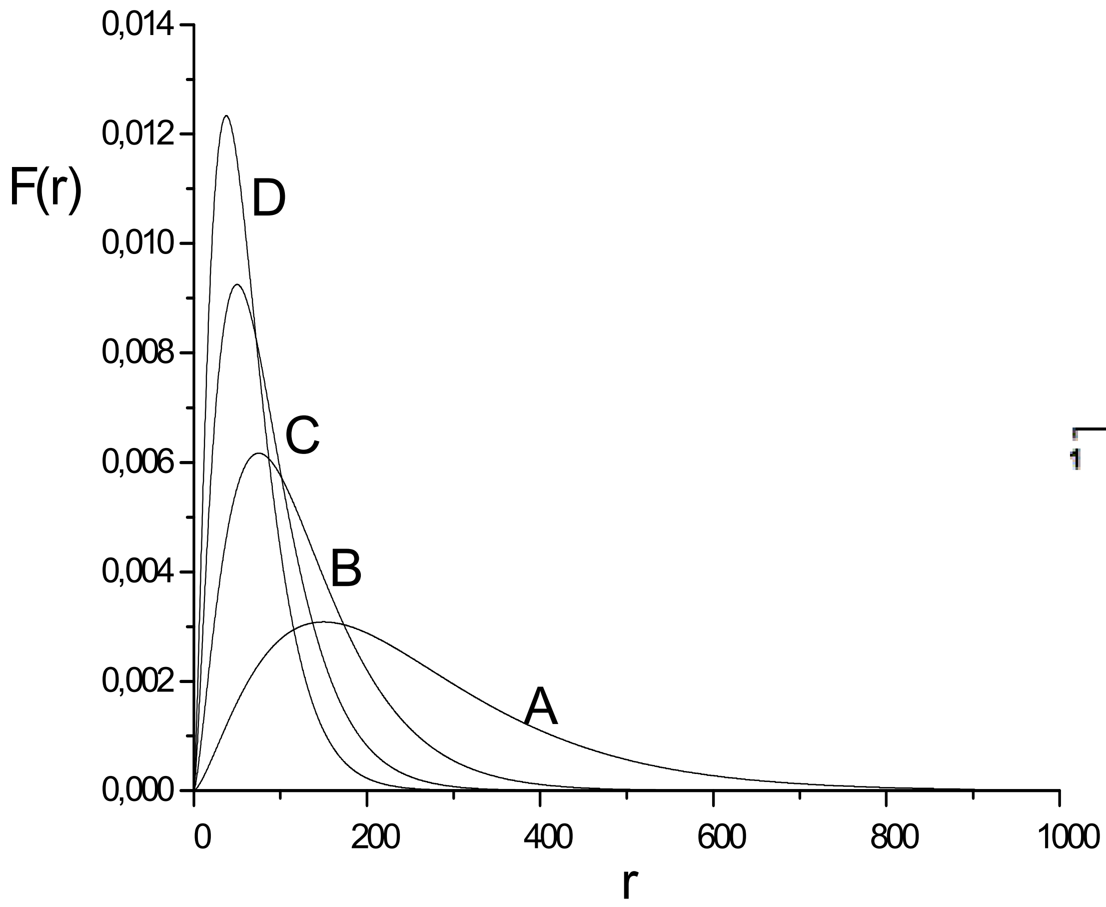
Microscopically – discrete
Macroscopically – continuous

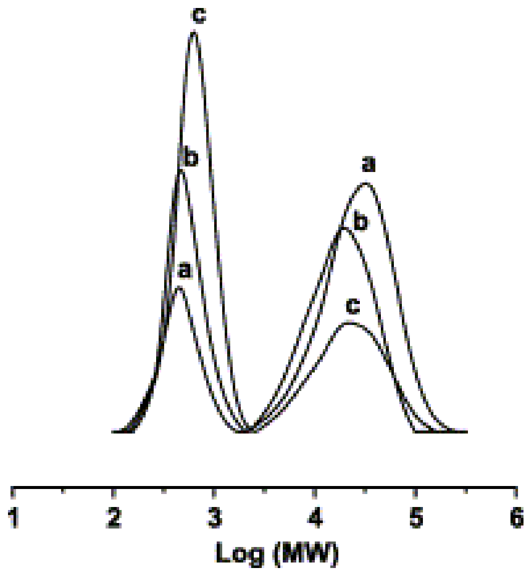


Determination of molecular weight of polymers

Molecular weight distributions

Unimodal
Tailing towards the high-molecular weight end



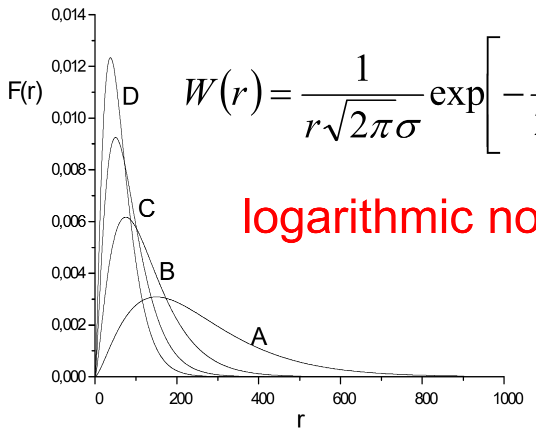


Bimodal distribution

Determination of molecular weight of polymers

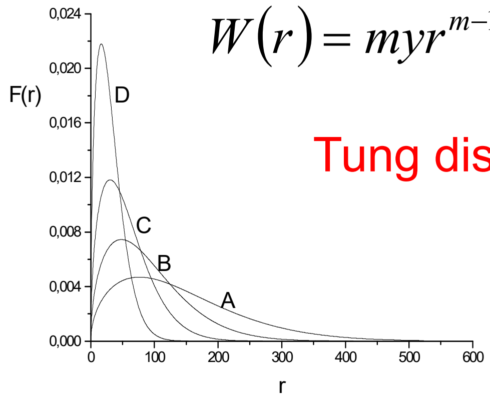
Molecular weight distributions

Some distribution functions



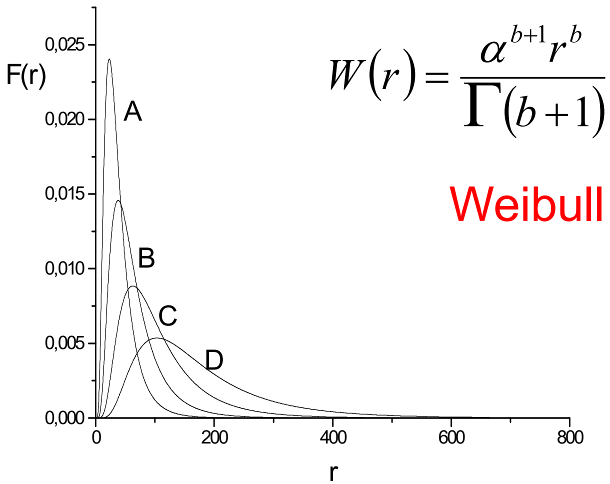
$$W(r) = \frac{1}{r\sqrt{2\pi}\sigma} \exp\left[-\frac{1}{2} \left(\frac{\ln r - \ln \bar{r}_m}{\sigma} \right)^2 \right]$$

logarithmic normal distribution



$$W(r) = myr^{m-1} \exp\left(-yr^m\right)$$

Tung distribution



$$W(r) = \frac{\alpha^{b+1} r^b}{\Gamma(b+1)} \exp(-\alpha r)$$

Weibull distribution

Determination of molecular weight of polymers

Molecular weight averages

Number average molecular weight	Weight average molecular weight	*z*-average molecular weight
$\bar{r}_n = \dfrac{\int_0^\infty rF(r)dr}{\int_0^\infty F(r)dr}$	$\bar{r}_w = \dfrac{\int_0^\infty r^2F(r)dr}{\int_0^\infty rF(r)dr}$	$\bar{r}_z = \dfrac{\int_0^\infty r^3F(r)dr}{\int_0^\infty r^2F(r)dr}$
$\bar{r}_n = \dfrac{\int_0^\infty W(r)dr}{\int_0^\infty \frac{W(r)dr}{r}}$	$\bar{r}_w = \dfrac{\int_0^\infty rW(r)dr}{\int_0^\infty W(r)dr}$	$\bar{r}_z = \dfrac{\int_0^\infty r^2W(r)dr}{\int_0^\infty rW(r)dr}$
$\overline{M}_n = \bar{r}_n \cdot M_0$	$\overline{M}_w = \bar{r}_w \cdot M_0$	$\overline{M}_z = \bar{r}_z \cdot M_0$

What would be the formulae for r_{z+1}?

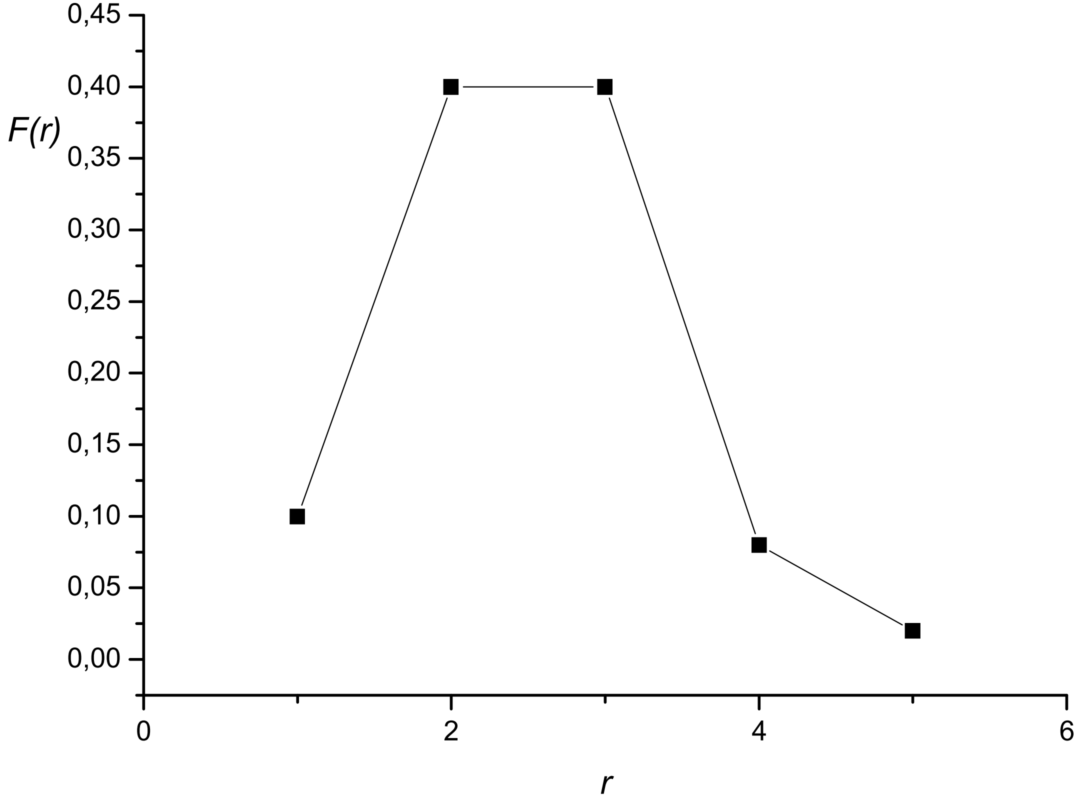
Dispersity, *Đ* (obsolete: Polydispersity index) measure of the distribution (relative) width

$$Đ = \overline{M}_w / \overline{M}_n$$

EXAMPLE 1

Distribution

r	1	2	3	4	5
F(r)	0,1	0,4	0,4	0,08	0,02



EXAMPLE 1

Distribution

r	1	2	3	4	5
$F(r)$	0,1	0,4	0,4	0,08	0,02

Number average:

$$\bar{r}_n = \frac{\int_0^\infty rF(r)dr}{\int_0^\infty F(r)dr} \qquad \bar{r}_n = \frac{\sum_1^5 rF(r)}{\sum_1^5 F(r)} = \frac{1\cdot 0{,}1 + 2\cdot 0{,}4 + 3\cdot 0{,}4 + 4\cdot 0{,}08 + 5\cdot 0{,}02}{1} = 2{,}52$$

Weight average:

$$\bar{r}_w = \frac{\int_0^\infty r^2F(r)dr}{\int_0^\infty rF(r)dr} \qquad \bar{r}_w = \frac{\sum_1^5 r^2F(r)}{\sum_1^5 rF(r)} = \frac{1^2\cdot 0{,}1 + 2^2\cdot 0{,}4 + 3^2\cdot 0{,}4 + 4^2\cdot 0{,}08 + 5^2\cdot 0{,}02}{1\cdot 0{,}1 + 2\cdot 0{,}4 + 3\cdot 0{,}4 + 4\cdot 0{,}08 + 5\cdot 0{,}02} = \frac{7{,}08}{2{,}52} = 2{,}81$$

z-average:

$$\bar{r}_z = \frac{\int_0^\infty r^3F(r)dr}{\int_0^\infty r^2F(r)dr} \qquad \bar{r}_z = \frac{\sum_1^5 r^3F(r)}{\sum_1^5 r^2F(r)} = \frac{1^3\cdot 0{,}1 + 2^3\cdot 0{,}4 + 3^3\cdot 0{,}4 + 4^3\cdot 0{,}08 + 5^3\cdot 0{,}02}{1^2\cdot 0{,}1 + 2^2\cdot 0{,}4 + 3^2\cdot 0{,}4 + 4^2\cdot 0{,}08 + 5^2\cdot 0{,}02} = \frac{21{,}72}{7{,}08} = 3{,}07$$

Example 1

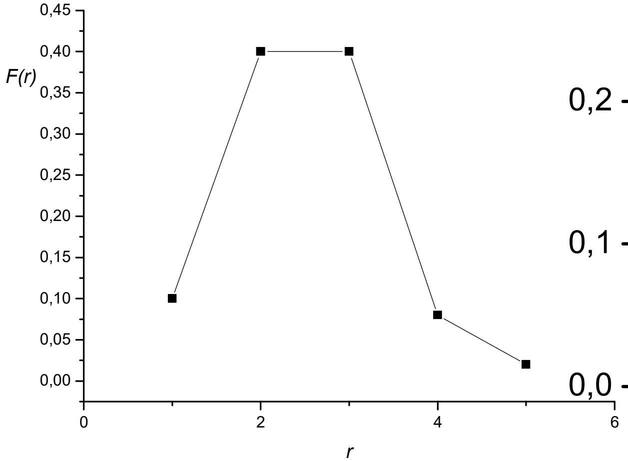
Distribution

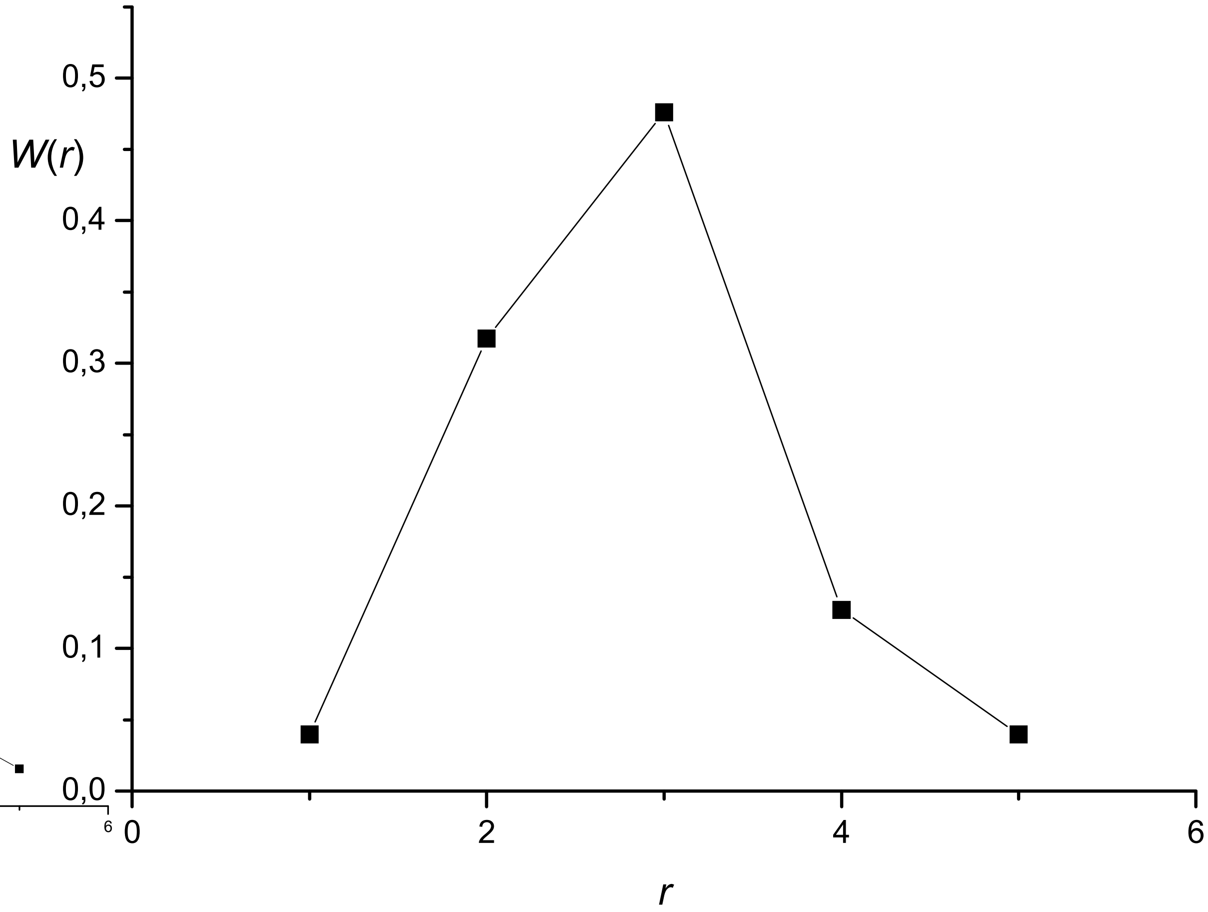
r	1	2	3	4	5
F(r)	0,1	0,4	0,4	0,08	0,02
W(r)	0,03968	0,31746	0,47619	0,12698	0,03968

Weight average:

$$W(r) = \frac{rF(r)}{\int_0^\infty rF(r)dr}$$

$$W(r) = \frac{rF(r)}{\sum_1^5 rF(r)} = \frac{rF(r)}{2,52}$$





Example 1

Distribution

r	1	2	3	4	5
F(r)	0,1	0,4	0,4	0,08	0,02
W(r)	0,03968	0,31746	0,47619	0,12698	0,03968

Weight average:

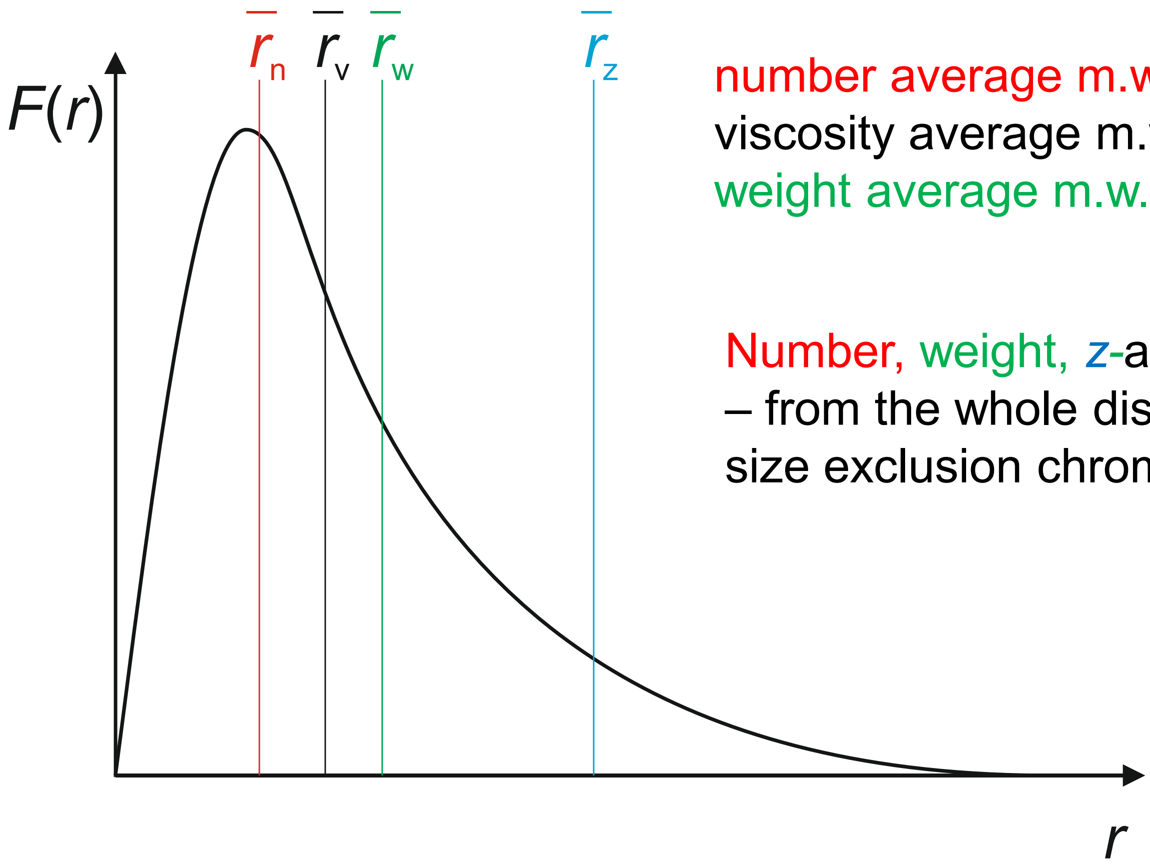
$$\bar{r}_w = \frac{\int_0^\infty rW(r)dr}{\int_0^\infty W(r)dr} \qquad \bar{r}_w = \frac{\sum_1^5 rW(r)}{\sum_1^5 W(r)} = \frac{2{,}81}{1} = 2{,}81$$

Number average:

$$\bar{r}_n = \frac{\int_0^\infty W(r)dr}{\int_0^\infty \frac{W(r)dr}{r}} \qquad \bar{r}_n = \frac{\sum_1^5 W(r)}{\sum_1^5 \frac{W(r)}{r}} = \frac{1}{0{,}39683} = 2{,}52$$

Determination of molecular weight of polymers

Molecular weight averages



number average m.w. – from colligative properties
viscosity average m.w. – from viscometry
weight average m.w. – from light scattering

Number, weight, *z*-average m.w.
– from the whole distribution as obtained by size exclusion chromatography

Determination of molecular weight of polymers

Experimental methods

Absolute methods:

mass spectrometry
colligative properties
end group analysis
light scattering
ultracentrifugation

Relative methods

solution viscosity

Fractionation methods (relative methods, too!)

size exclusion chromatography (SEC)
or (obsolete) gel permeation chromatography (GPC)

Absolute methods:
the measurement is directly related to M.W. (regardless of the polymer type)
end group analysis is an exemption

Relative methods
The quantity measured depends on the polymer structure – calibration is necessary
(which is unfortunately often forgotten)

Determination of molecular weight of polymers

Experimental methods

Method	Type	M.W. range	M.W. average
Ebullioscopy	Absolute (colligative)	$< 10^4$	M_n
Cryoscopy	Absolute (colligative)	$< 10^4$	M_n
Vapor pressure osmometry	Absolute (colligative)	$< 10^4$	M_n
Membrane osmometry	Absolute (colligative)	$< 10^5$	M_n
Mass spectrometry	Absolute	low M.W.	M_n
End group analysis	Absolute	$< 10^5$	M_n
Static light scattering	Absolute	$10^4 – 10^7$	M_w
Sedimentation equilibrium	Absolute	$< 10^6$	M_w M_z M_{z+1}
Sedimentation in a density gradient	Absolute	$> 10^5$	
Sedimentation velocity / diffusion	Absolute	$10^3 – 10^8$	
Solution viscosity	Relative	$10^2 – 10^8$	M_v
Size exclusion chromatography	Relative	$10^2 – 10^7$	detector dependent

Determination of molecular weight of polymers

End-group analysis

$M_n < 10^5$ (< 50000)

End-group must have detectable species

- vinyl polymers : -CX=CYZ
  (not all vinyl polymerizations are capable to produce such groups)
- polyesters: -COOH, -OH
- polyamides: -COOH, $-NH_2$
- polyurethanes: -OH, -NCO
- radioactive isotopes
- UV, IR, NMR detectable functional groups

- method cannot be applied to branched polymers
- in case of same end groups, divide the concentration with 2
- in case of different end groups, the concentration of end groups is equal to the concentration of polymers
- it is necessary to know the mechanism used to produce the polymer chains

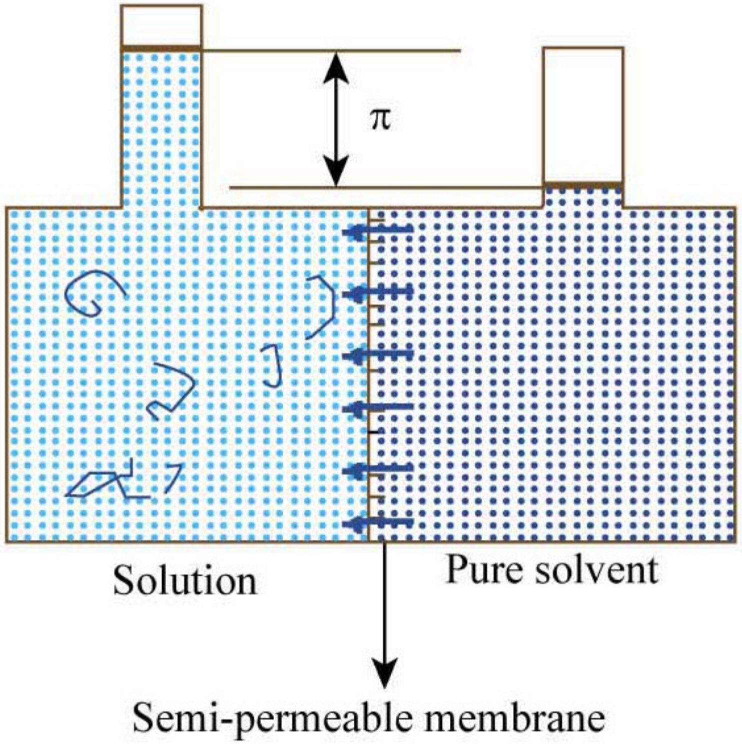
- limitation: high viscosity of polymer solutions makes mixing difficult

Determination of molecular weight of polymers

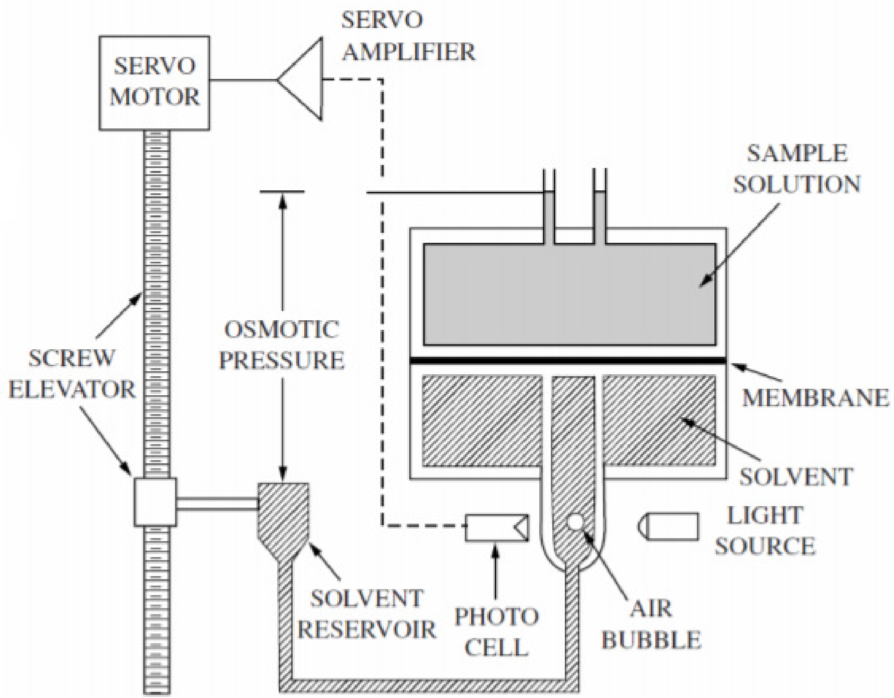
Membrane osmometry

$M_n < 10^5$ (< 50000)

Static apparatus
Equilibrium is
to be reached!



Dynamic apparatus
Flow of solvent is detected!

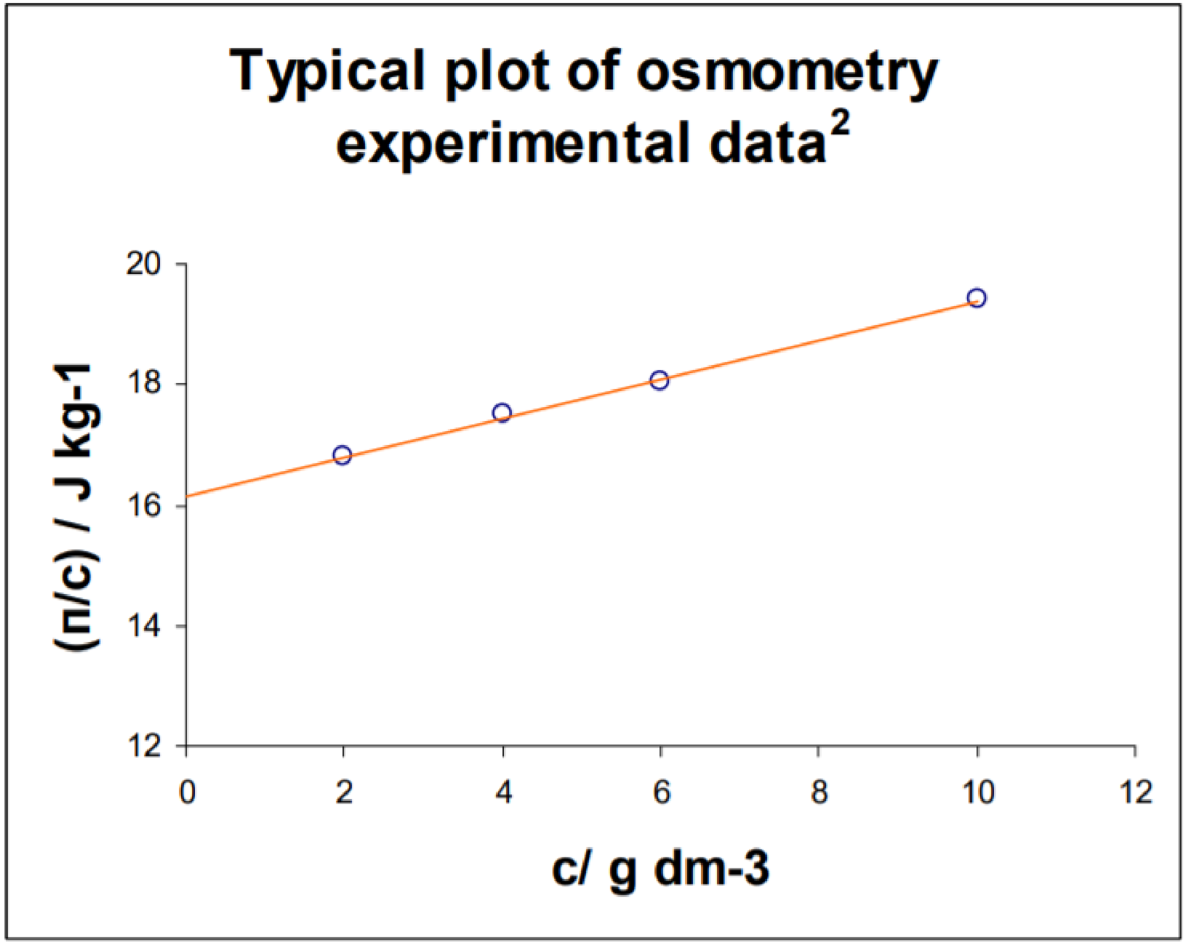


- limitation: low M.W. molecules (oligomers) passing through membrane

Determination of molecular weight of polymers

Membrane osmometry

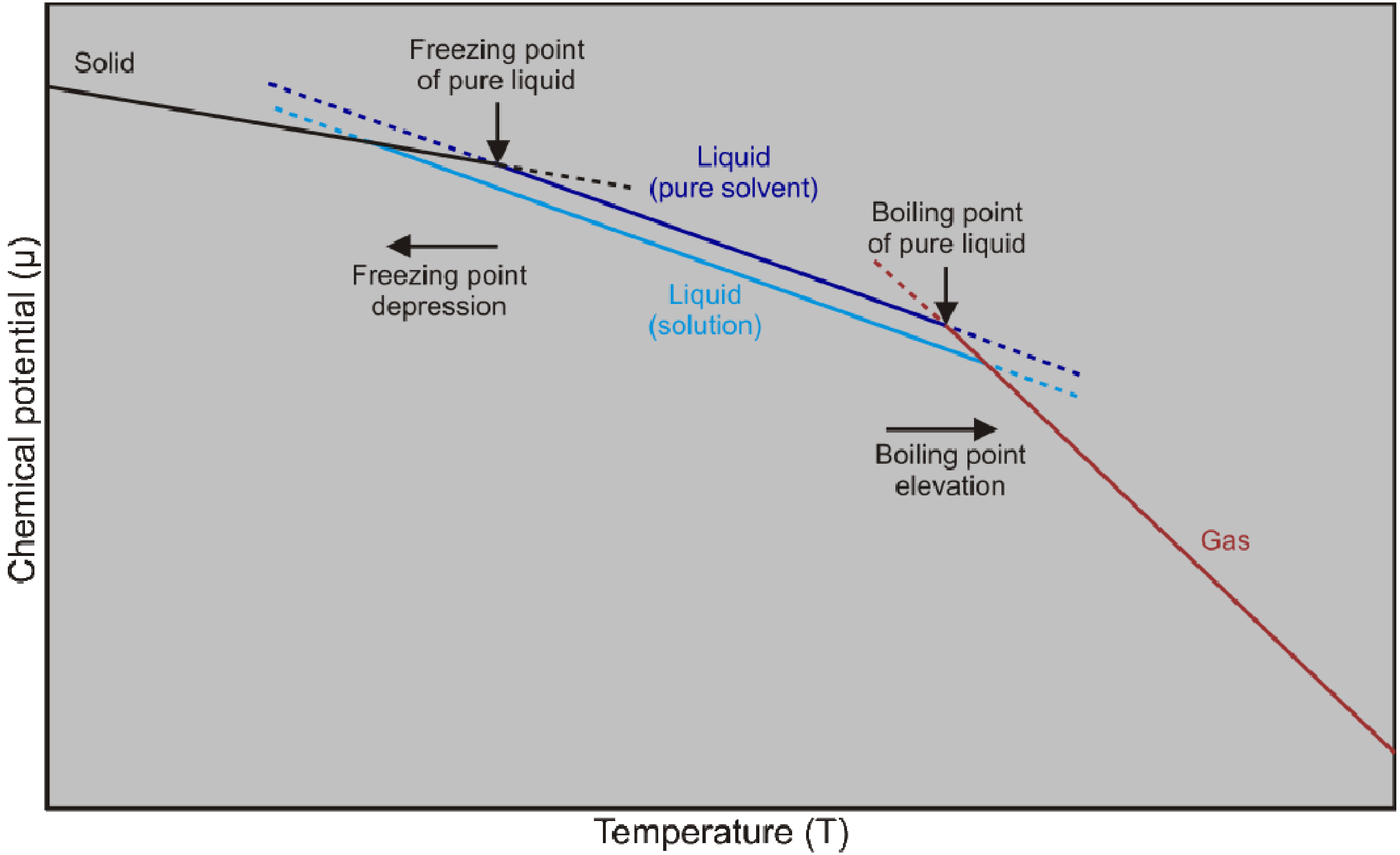
$$\frac{\pi}{c} = RT\left(\frac{1}{\bar{M}_n} + A_2 c + A_3 c^2 + \ldots\right)$$



Determination of molecular weight of polymers

Cryoscopy and ebullioscopy

$M_n < 10^4$ (< 20000)



Determination of molecular weight of polymers

Cryoscopy and ebullioscopy

$M_n < 10^4$ (< 20000)

Cryoscopy

$$\frac{\Delta T^f}{c} = K_c\left(\frac{1}{\bar{M}_n} + A_2 c + A_3 c^2 + \ldots\right)$$

Ebullioscopy

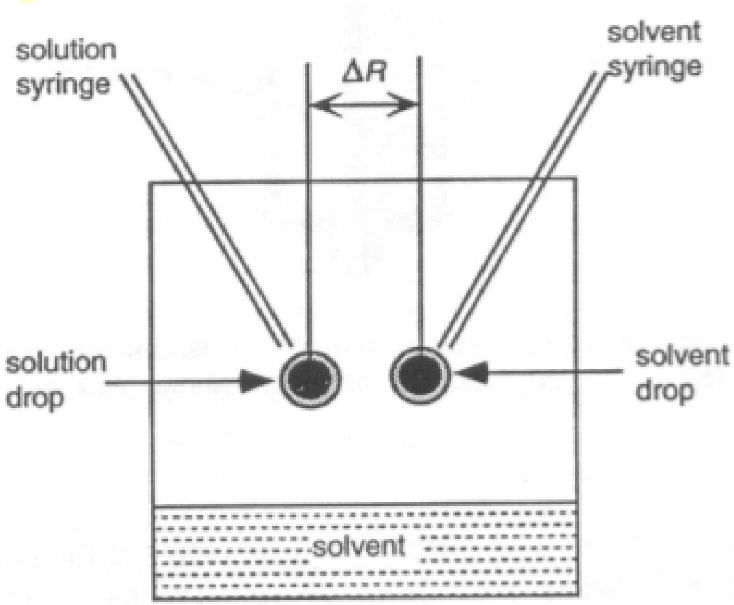
$$\frac{\Delta T^b}{c} = K_e\left(\frac{1}{\bar{M}_n} + A_2 c + A_3 c^2 + \ldots\right)$$

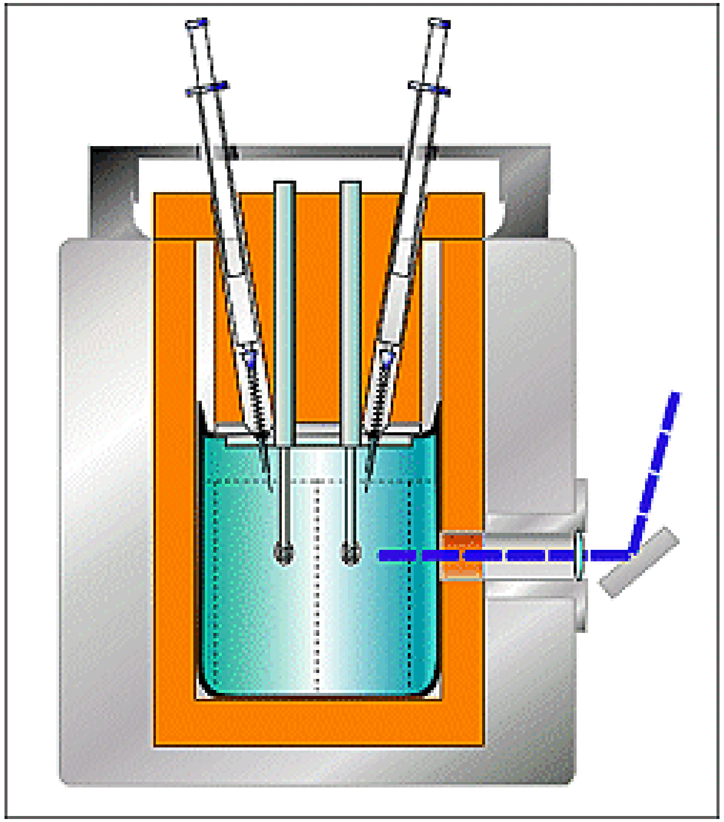
- limitation: temperature precision
- out-of-date method

Determination of molecular weight of polymers

Vapor pressure osmometry
(vapor phase osmometry)

$M_n < 10^4$ (< 30000)





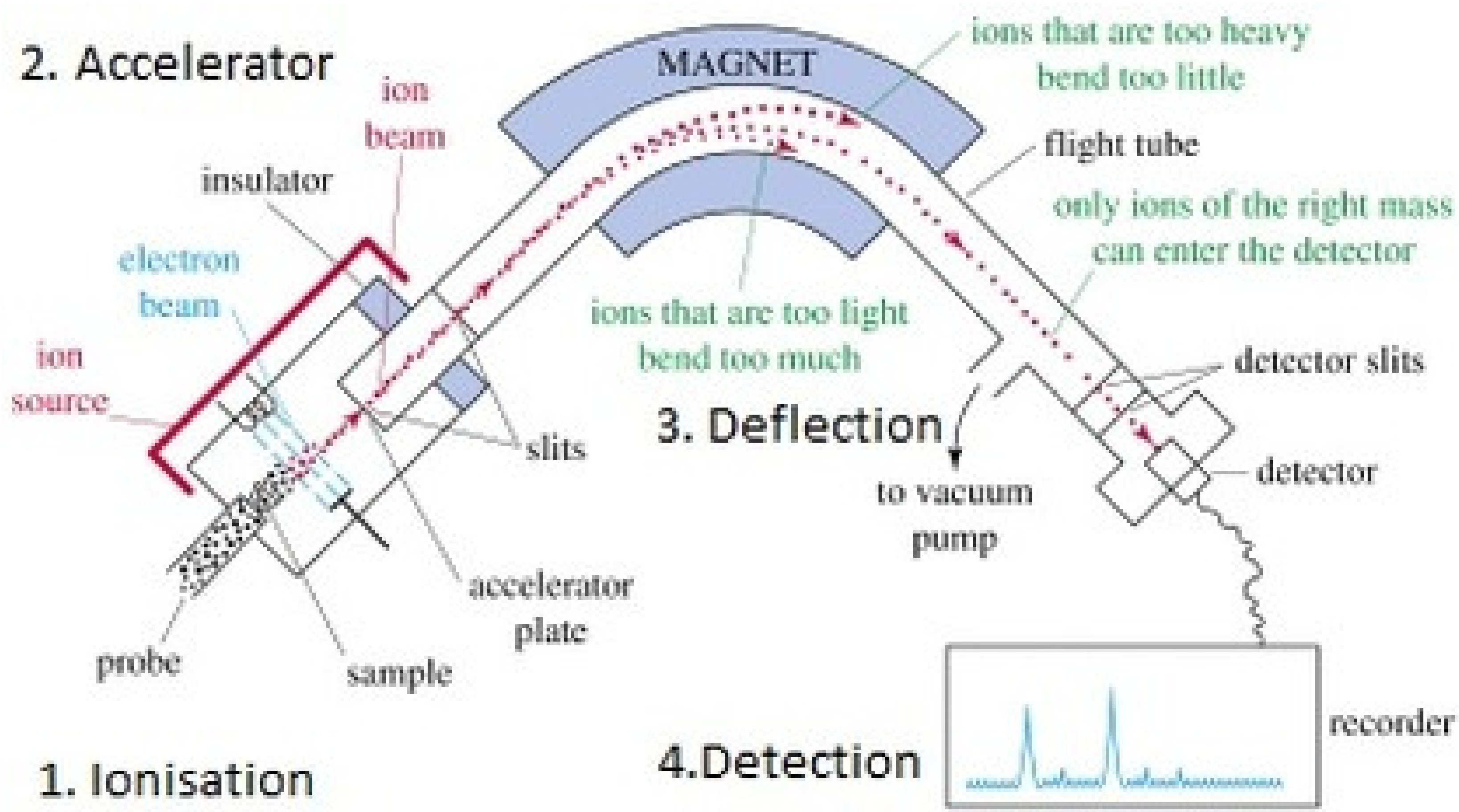
$$\Delta p = p - p^{\bullet} \qquad \Delta p \rightarrow \Delta T \rightarrow \Delta r \rightarrow \Delta U$$

$$\frac{\Delta r}{c} = K_{\mathrm{VPO}}\left(\frac{1}{\bar{M}_{\mathrm{n}}} + A_2 c + A_3 c^2 + \ldots\right)$$

Determination of molecular weight of polymers

Mass spectrometry

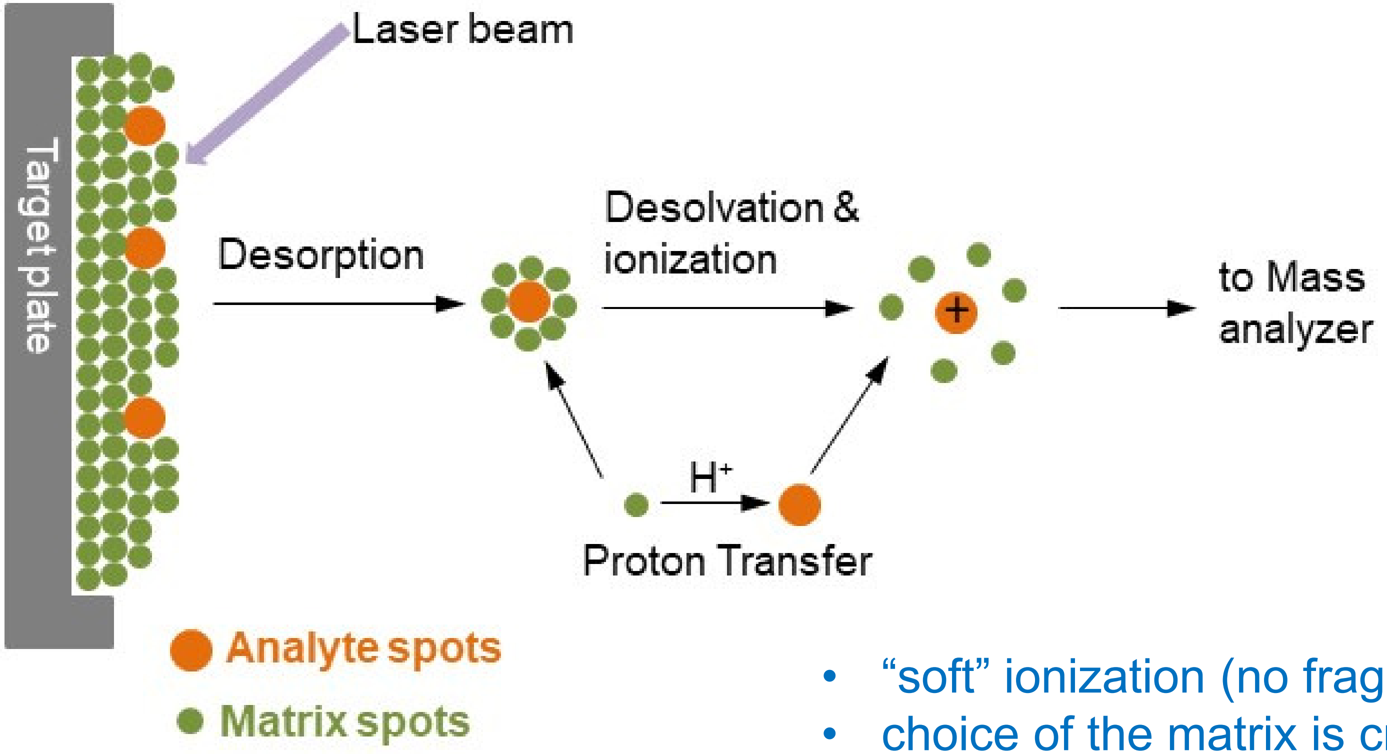
Relatively low M.W. polymers



Determination of molecular weight of polymers

Mass spectrometry

Relatively low M.W. polymers [but up to 400000 for uniform (natural) polymers]

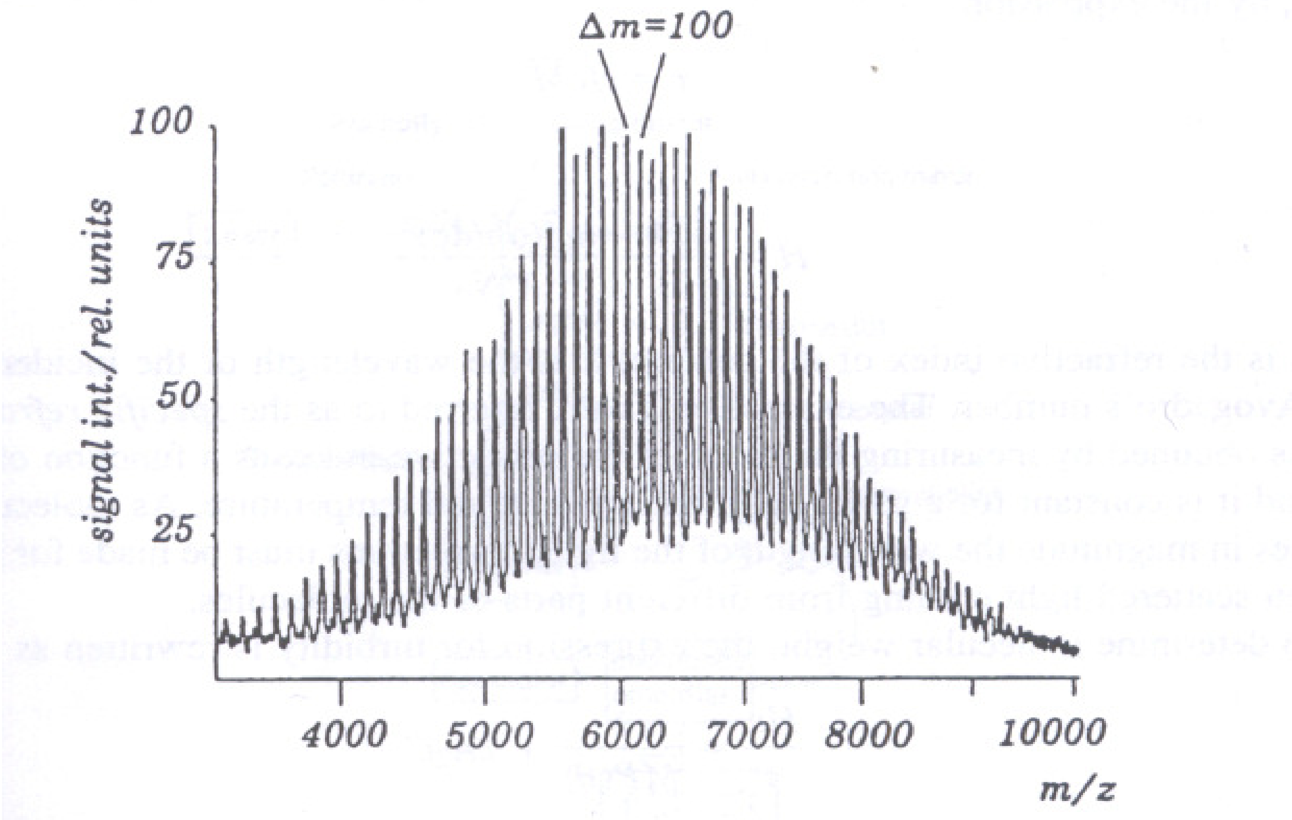


- “soft” ionization (no fragmentation)
- choice of the matrix is critical
- useful for (highly) branched polymers

MALDI-TOF
matrix-assisted laser desorption/ionization
time-of-flight spectrometer (high M.W. range)

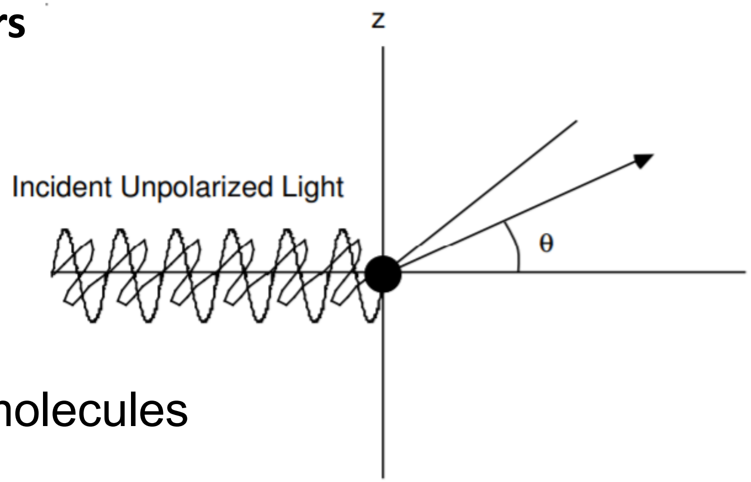
Determination of molecular weight of polymers

Mass spectrometry



Low molecular weight PMMA

Determination of molecular weight of polymers



(Static) Light scattering

$10^2 < M_w < 10^8$

The intensity of scattered light
or turbidity(τ) depends on:

- size (volume, mass) of the dissolved molecules
- concentration of the solution
- polarizability of the molecule
- refractive index of the solvent
- scattering angle
- solvent and solute interaction

K – characteristic constant of the system
c – concentration
R_θ^0 – Rayleigh ratio
r – observation distance
I_0 – incident light intensity
i_θ^0 – scattered light intensity
n_0 – refractive index of solvent
dn_0/dc – refractive index increment
λ – wavelength of incident light
N_A – Avogadro's number

Characteristic power series

$$\frac{Kc}{R_\theta^0} = \frac{1}{\bar{M}_w} + 2A_2c + 3A_3c^2 + \dots$$

$$K = \frac{2\pi^2 n_0^2}{\lambda^4 N_A}\left(\frac{dn_0}{dc}\right)^2$$

$$R_\theta^0 = \frac{r^2 i_\theta^0}{I_0}$$

Determination of molecular weight of polymers

Light scattering

$10^4 < M_w < 10^7$

θ – scattering angle

Zimm plot

$$\frac{Kc}{R_\theta^0} = \left(\frac{1}{\bar{M}_w} + 2A_2c\right)\left(1 + \frac{16\pi^2}{3\lambda^2}\langle s^2\rangle_w \sin^2\frac{\theta}{2}\right)$$

First extrapolation – (Kc/R) vs. $\sin^2(\theta/2)$ at c = const

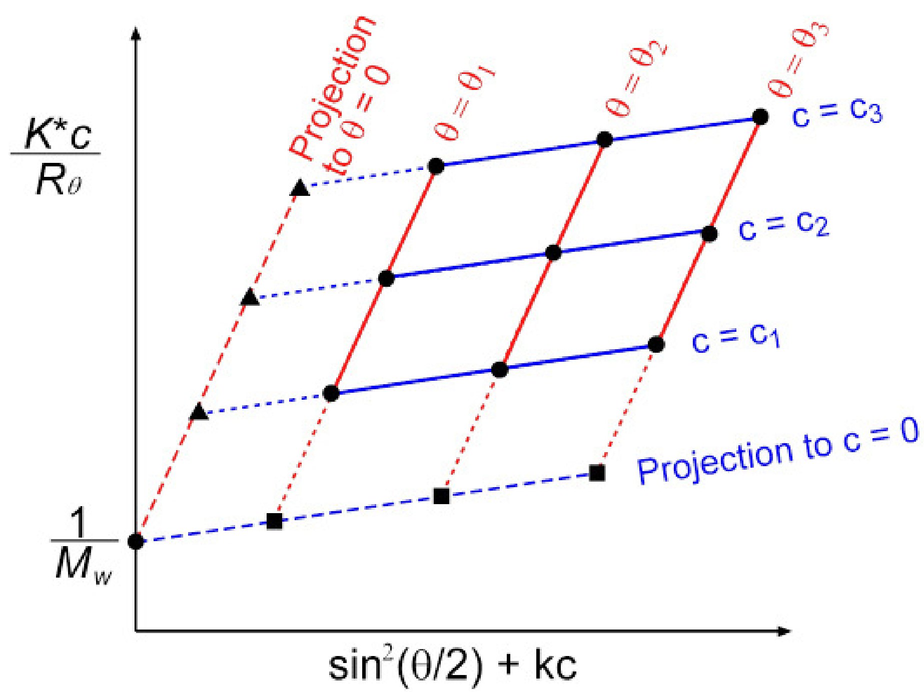
$$\text{slope} = \left(\frac{1}{\bar{M}_w} + 2A_2c\right)\frac{16\pi^2}{3\lambda^2}\langle s^2\rangle_w$$

$$\text{intercept} = \left(\frac{1}{\bar{M}_w} + 2A_2c\right)$$

Second extrapolation – intercept *vs. c*

$$\text{slope} = 2A_2$$

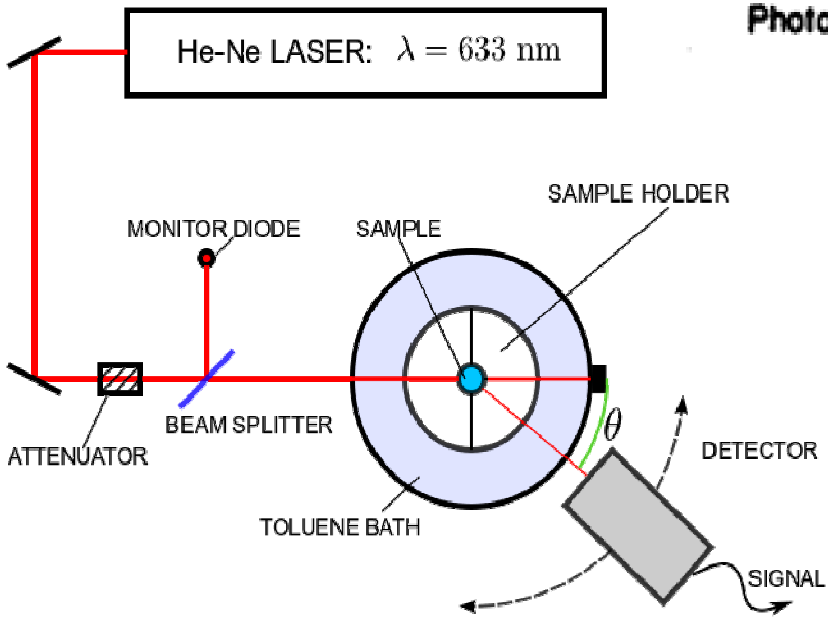
$$\text{intercept} = \frac{1}{\bar{M}_w}$$

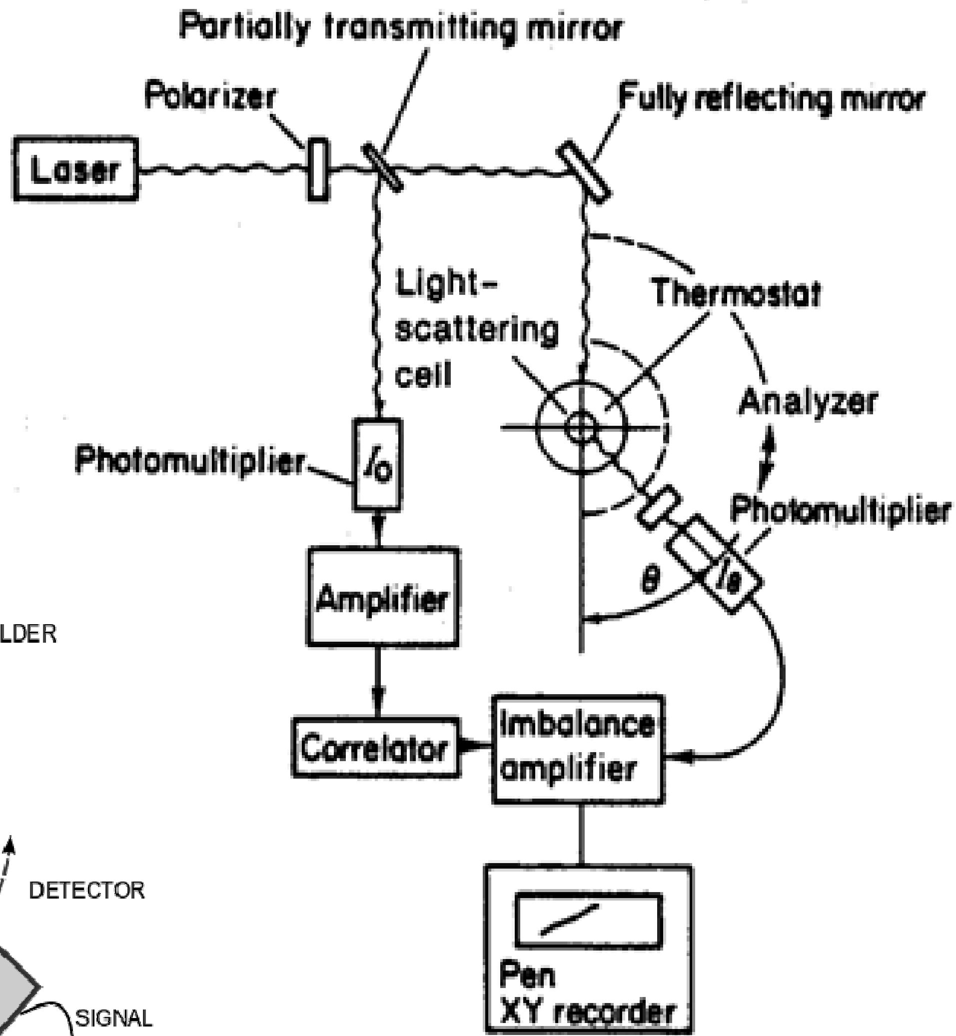


Determination of molecular weight of polymers

Light scattering

$10^4 < M_w < 10^7$





Determination of molecular weight of polymers

Ultracentrifugation

M_z is determined

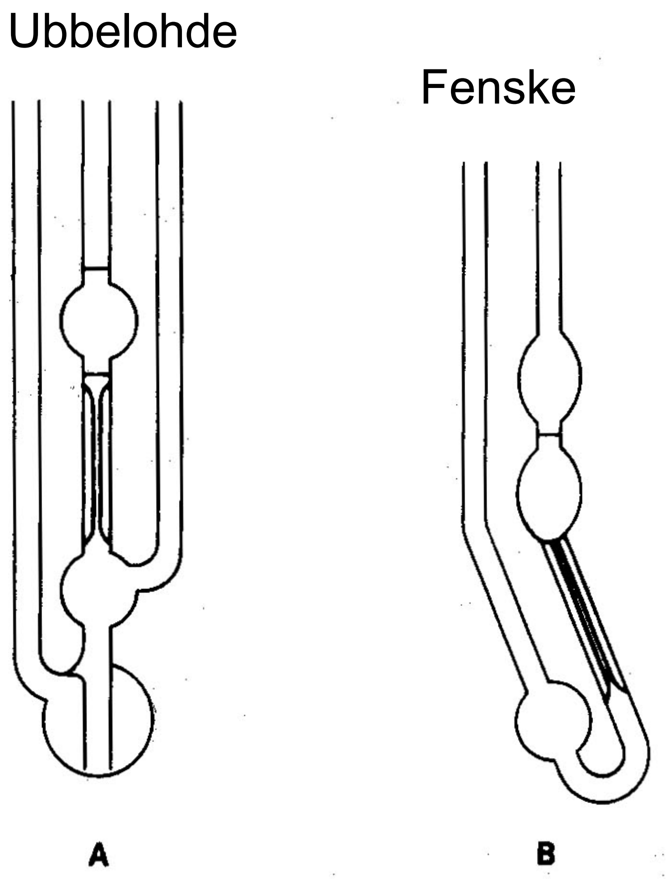
- used primarily for proteins
- molecules are distributed in the centrifugal field according to their size
- the process is performed until sedimentation equilibrium is reached

Determination of molecular weight of polymers

Viscometry

M_v is determined

- capillary viscometers
- flowing time is measured



η – solution viscosity
η_0 – solvent viscosity
t – solution flowing time
t_0 – solvent flowing time

relative viscosity $$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0}$$

specific viscosity $$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_{rel} - 1$$

reduced viscosity $$\eta_{red} = \frac{\eta_{sp}}{c} = \frac{\eta_{rel} - 1}{c}$$

inherent viscosity $$\eta_{inh} = \frac{\ln \eta_{rel}}{c}$$

intrinsic viscosity $$[\eta] = \lim_{c \to 0} \eta_{red} = \lim_{c \to 0} \eta_{inh}$$

Determination of molecular weight of polymers

Viscometry

M_v is determined

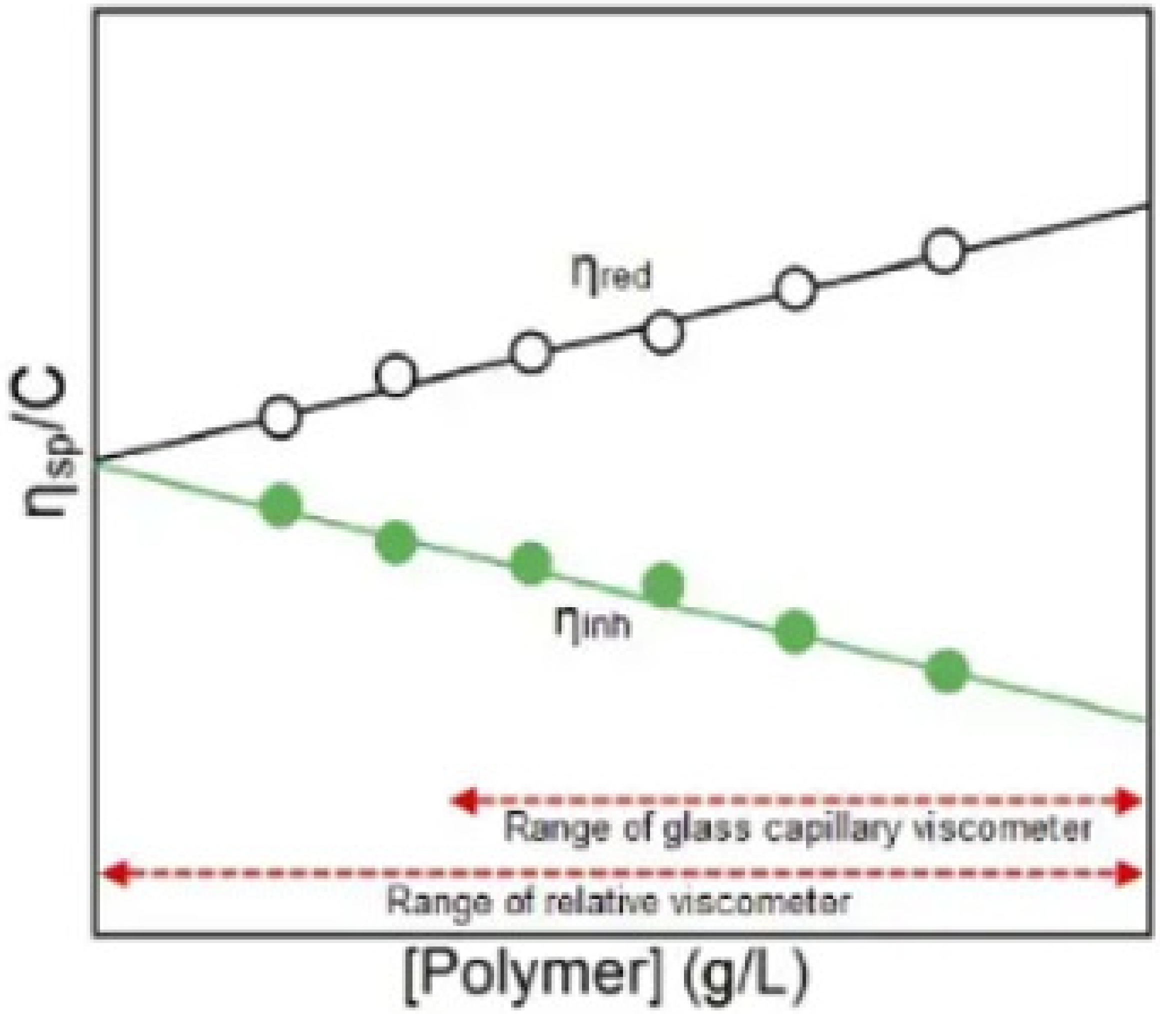


Figure 3: The Huggins/Kraemer Plot.

Determination of molecular weight of polymers

Viscometry

M_v is determined

Mark-Houwink-Sakurada equation

$$[\eta] = K\bar{M}^a$$

linearized form, *K* and *a* characteristic for a polymer-solvent pair

$$\log[\eta] = \log K + a \cdot \log \bar{M}$$

$$M_n < M_v < M_w$$ $\bar{M}_v$ is closer to $\bar{M}_w$ than to $\bar{M}_n$

Determination of molecular weight of polymers

Size exclusion chromatography
(gel permeation chromatography – obsolete term)

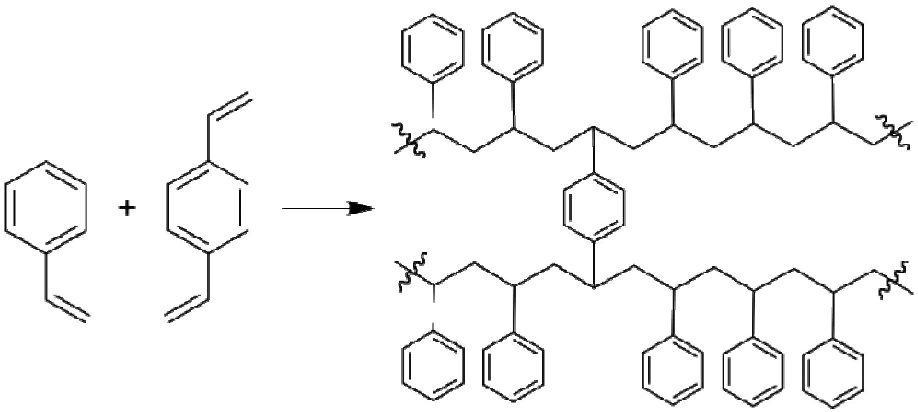
whole M.W. distribution is determined

- column chromatography
- packing material
  - poly(styrene-*co*-divinylbenzene) for nonpolar polymers
  - silica-based for polar polymers
  - swollen in a solvent
- detector
  - solution refractive index (RI)
  - UV absorption detector
  - IR absorption detector
  - LS (light scattering detector)
- chromatography pump
- injector
- collection of fractions is optional

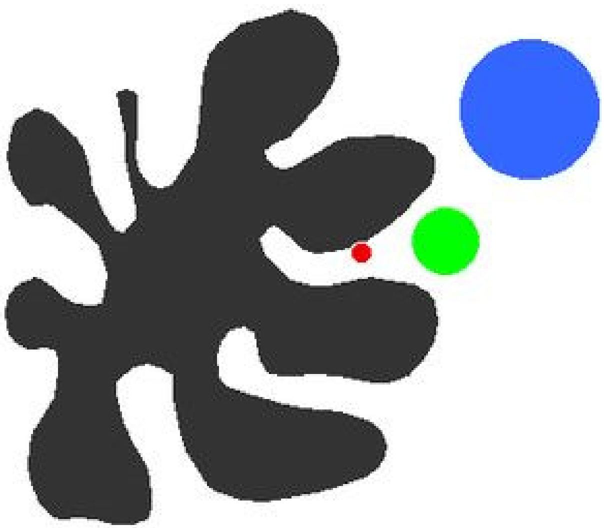
- Calibration is required – using very narrow M.W. polymer samples

Determination of molecular weight of polymers

Size exclusion chromatography



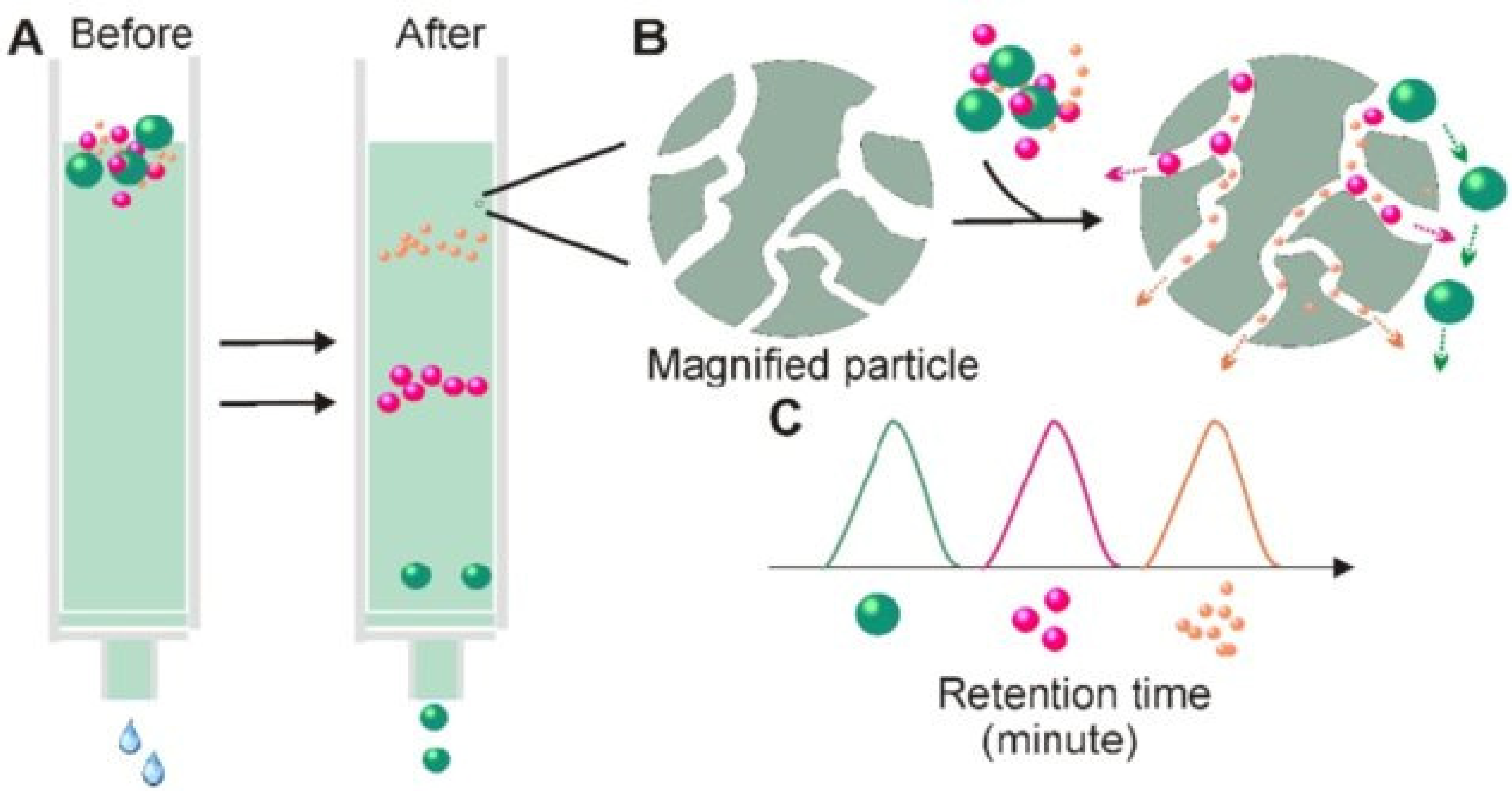
Gel material – beads of copolymer of styrene and divinylbenzene by suspension polymerization



swollen polymer gel
small molecules diffuse in all pores
the largest one do not diffuse at all

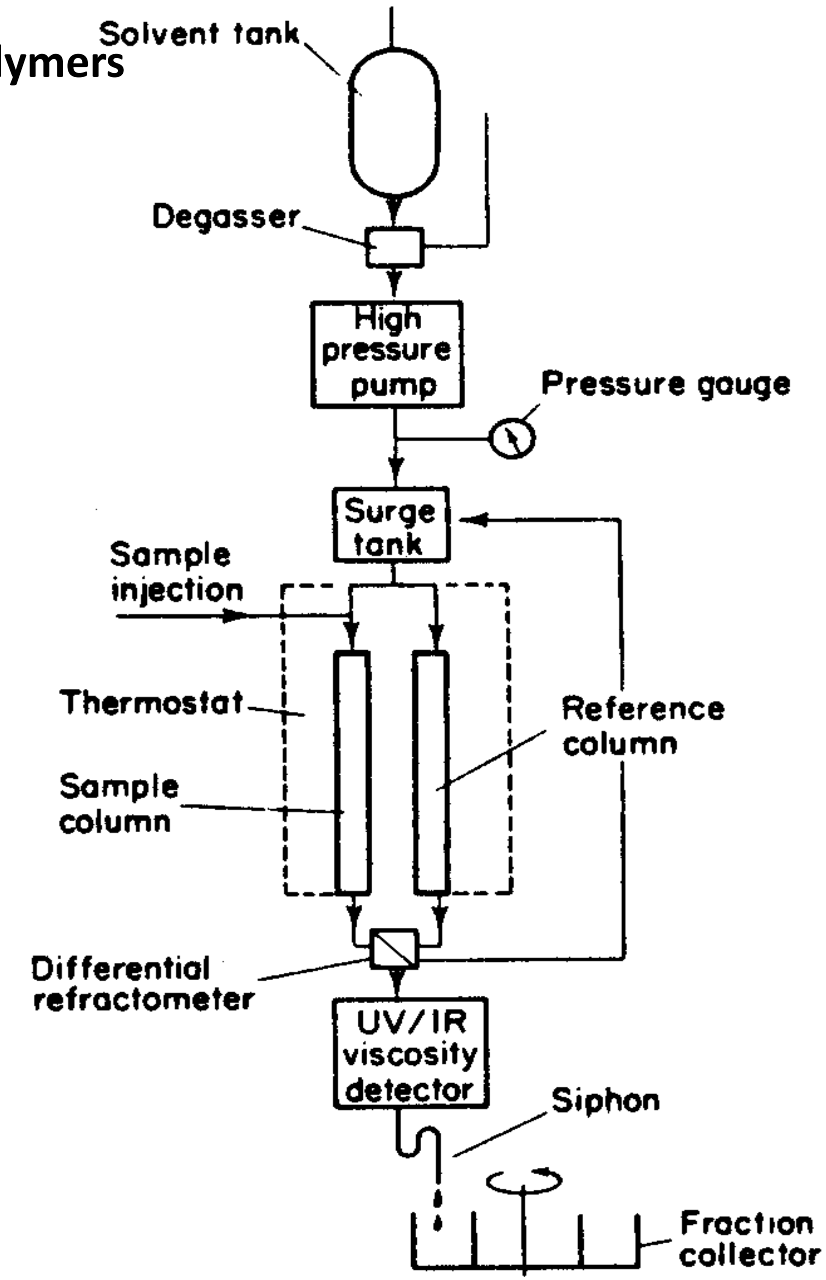
Determination of molecular weight of polymers

Size exclusion chromatography



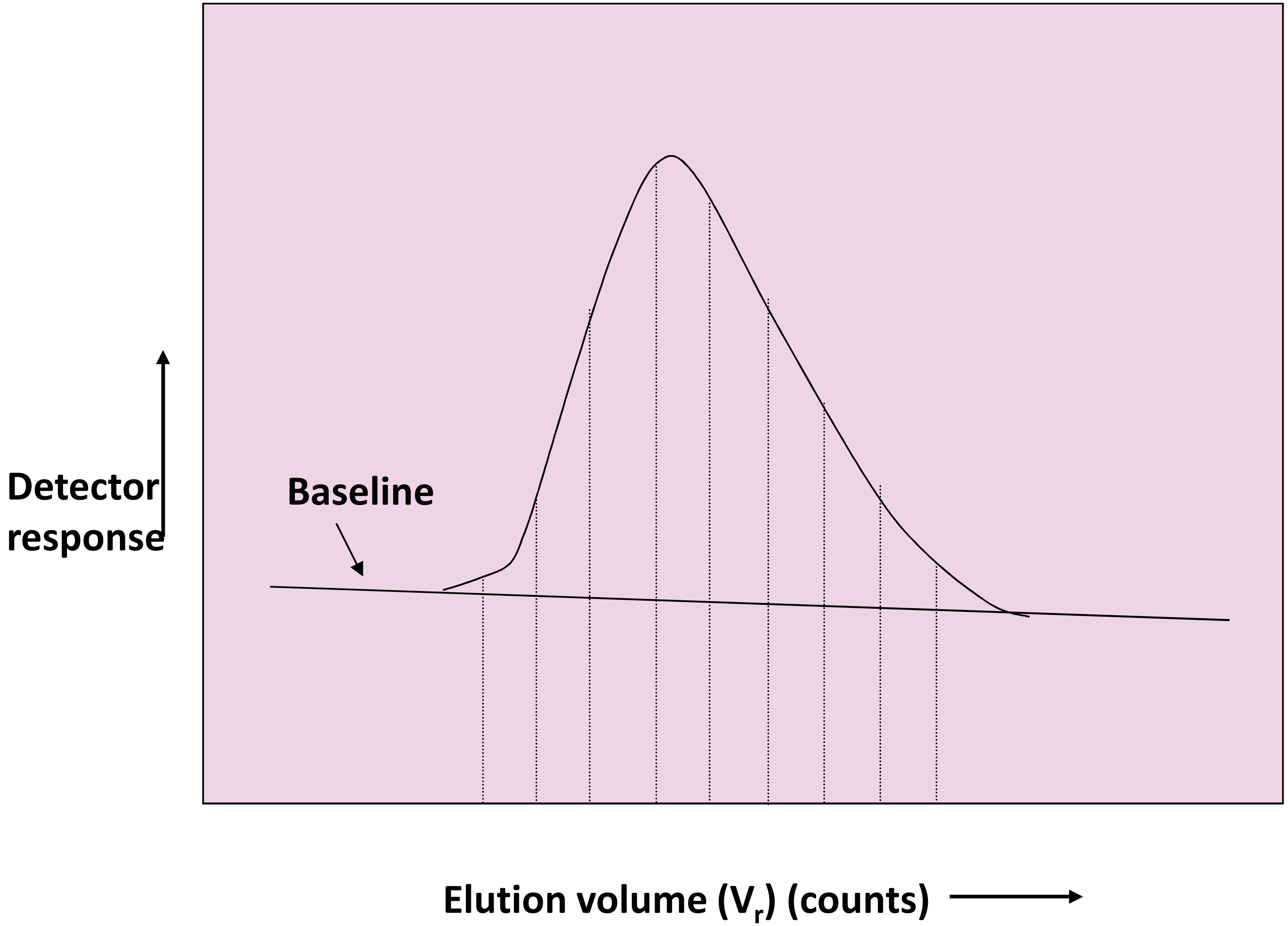
Determination of molecular weight of polymers

Size exclusion chromatography



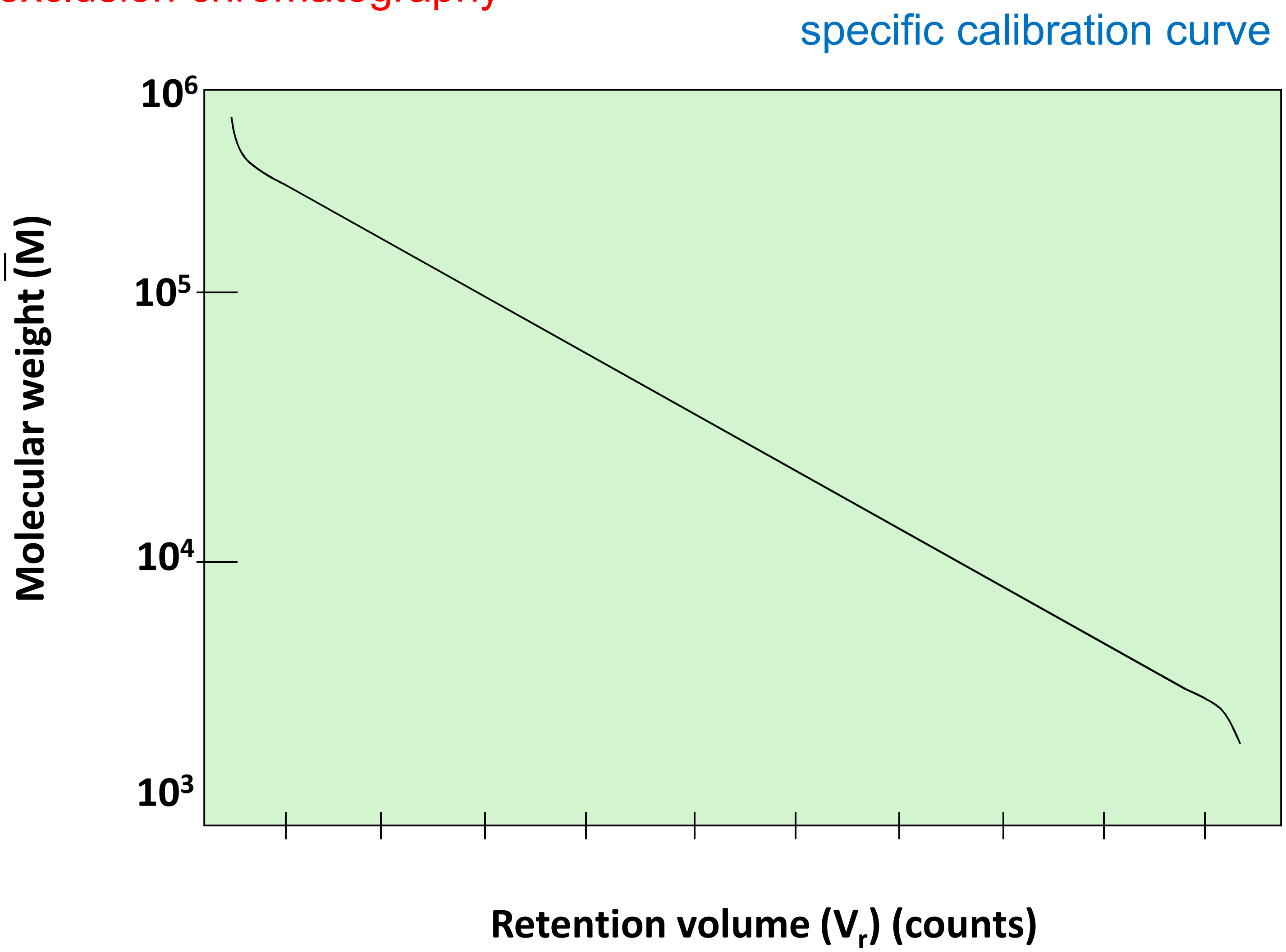
Determination of molecular weight of polymers

Size exclusion chromatography



Determination of molecular weight of polymers

Size exclusion chromatography

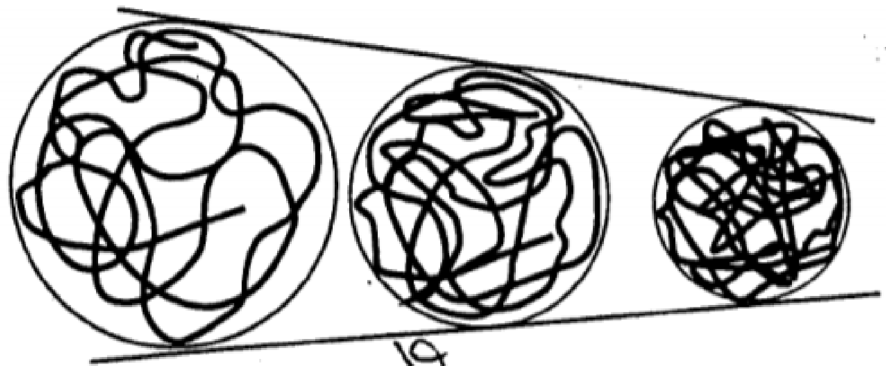


Determination of molecular weight of polymers

Size exclusion chromatography

Universal calibration mehod

- Typical calibration by PS standards
- Typical solvent is THF or toluene
- But PMMA has different interaction with solvents – different size of polymer coils for the same M.W.



- Hydrodynamic volume

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

$$\log M_2 = \frac{1}{1+a_2}\log\left(\frac{K_1}{K_2}\right) + \frac{1+a_1}{1+a_2}\log M_1$$

Determination of molecular weight of polymers

Size exclusion chromatography

Universal calibration method