UNESCO/IUPAC Postgraduate Course in Polymer Science

Lecture:

Molecular weight and dimensions of polymers and their assemblies

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Polymers

M gives independent information

M affects

properties such as density, degree of crystallization, Young modulus, melt viscosity, glass transition temperature etc

Consequently, *M* affects application use and processing methods

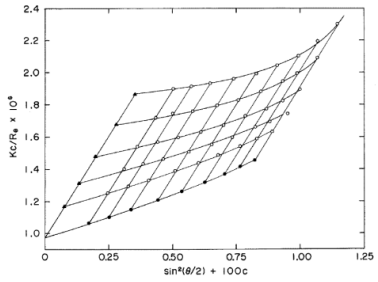
Classical methods for determination of molecular weight of polymers
(see Polymer solutions in a nutshell)

Osmotic pressure (absolute, 5 10^3-10^6)

$$\Pi_{c\to 0} = RT\ \frac{c}{M}$$

Static Light scattering (absolute, 10^4-10^7)

$$\left(\frac{Kc}{R_\theta}\right)_{c\to 0} = \frac{1}{M}\left[1+\frac{16\pi^2 n^2}{3\lambda}\left\langle R_g^2\right\rangle \sin^2\left(\frac{\theta}{2}\right)+\ldots\right]$$



Zimm plot (2 D plot for 2 independent variables) => M, A_2, R_g

Intrinsic viscosity (relative, >10^3)

$$[\eta] = KM^{a}$$ (Mark-Houwink Eq.)

And many more - analytical ultracentrifugation, ebullioscopy, end-group analysis, vapor pressure osmometry, ….

Polymer sample (usually) contains molecules of various polymerization degree

Experimental methods give us only some average of the molecular weight

$$\left(\frac{Y}{c}\right)_{c\to 0} = KM^{a} \qquad Y = \sum_i Y_i \qquad cK\overline{M}^{a} = \sum_i c_i K M_i^{a} \qquad \overline{M} = \left(\sum_i w_i M_i^{a}\right)^{\frac{1}{a}}$$

$$a_{\Pi} = -1 \qquad a_{\mathrm{LS}} = 1 \quad a_{\eta} = 0.5 - 0.8 \text{ flexible} > 0.8 \text{ rigid}$$

Averages with integer a can be defined as the ratio of moments around the origin

$$M_{\mathrm{n}} = \left(\sum_i w_i M_i^{-1}\right)^{-1} = \frac{\sum_i w_i M_i^{0}}{\sum_i w_i M_i^{-1}} \qquad M_{\mathrm{w}} = \sum_i w_i M_i = \frac{\sum_i w_i M_i^{1}}{\sum_i w_i M_i^{0}} \qquad M_{\mathrm{z}} = \frac{\sum_i w_i M_i^{2}}{\sum_i w_i M_i^{1}}$$

number-average weight-average z-average mol. weight

$$M_{\mathrm{n}} = \left(\sum_i x_i M_i\right)^{-1} = \frac{\sum_i x_i M_i^{1}}{\sum_i x_i M_i^{0}} \qquad M_{\mathrm{w}} = \frac{\sum_i x_i M_i^{2}}{\sum_i x_i M_i^{1}} \qquad M_{\mathrm{z}} = \frac{\sum_i x_i M_i^{3}}{\sum_i x_i M_i^{2}}$$

w weight fraction, *x* molar fraction

Combined averages give only partial information on the sample molecular weight non-uniformity : polydispersity index M_w/M_n

Full information:

relative amount of each polymerization degree – a distribution function

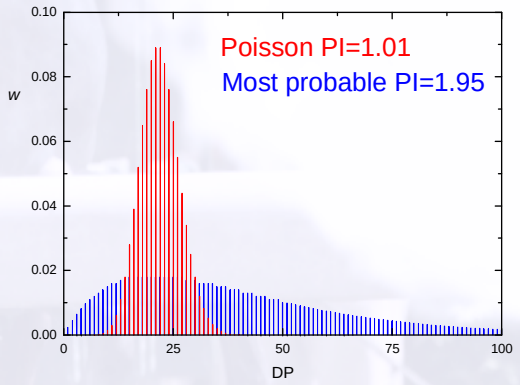
number DF - x_i, weight (mass) DF – w_i

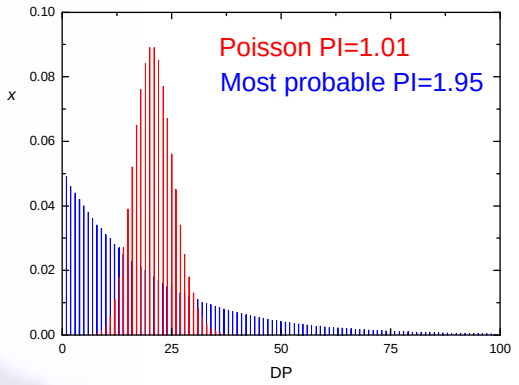
cumulative $\sum_{j=1}^{i} x_j$ $\sum_{j=1}^{i} w_i$ discrete vs continous DF

cumulative vs differential DF $\mathrm{difDF} = \frac{d\mathrm{cumDF}}{dM}$

Mathematically defined DF

Discrete DF Poisson $w_P = \frac{Pe^{-a}a^{P-1}}{(a+1)(P-1)!}$ most-probable $w_P = a^2P(1-a)^{P-1}$

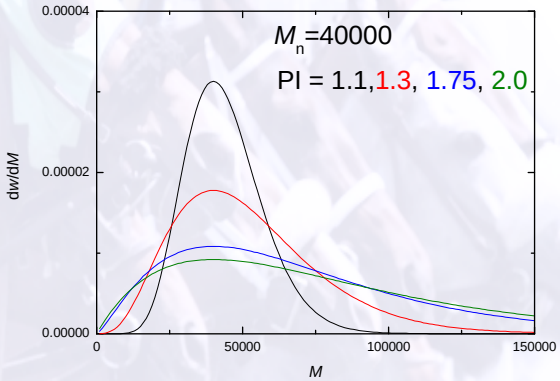


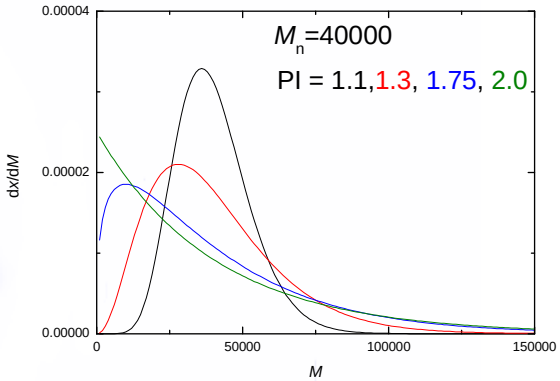


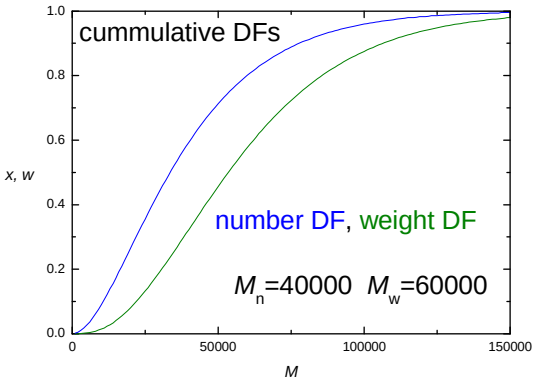
Continuous DF

Schulz-Zimm

$$dw = \frac{a^{b+1}}{\Gamma(b+1)} M^{b} \exp(-aM)\,dM$$

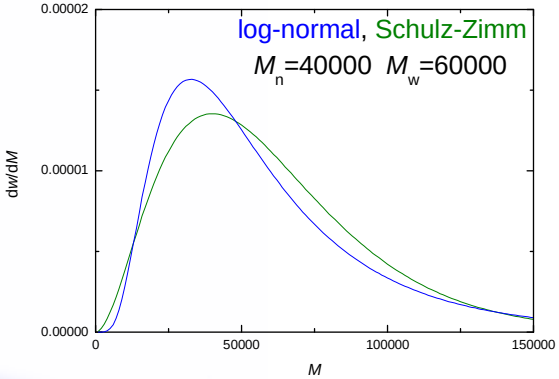




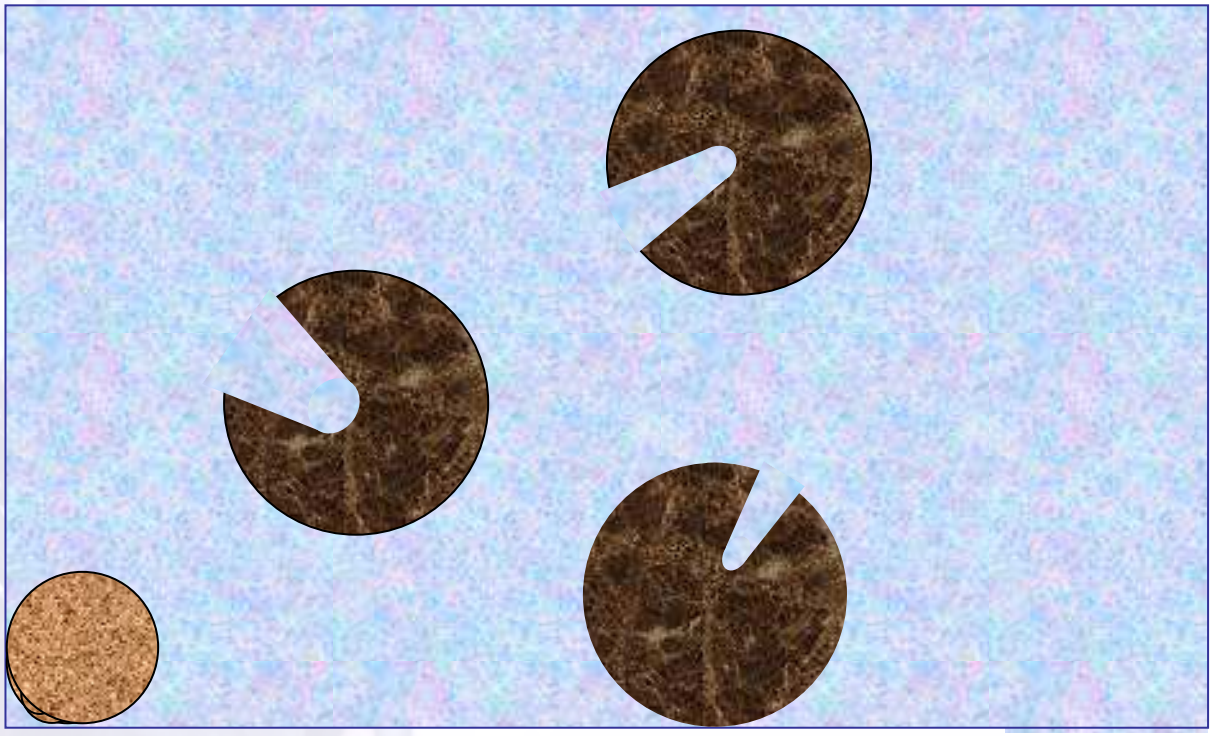


logarithmic normal

$$dw = \frac{1}{a\sqrt{\pi M}} \exp\left(-\frac{1}{a^{2}} \ln^{2} \frac{M}{b}\right) dM$$



Principle of Size Exclusion Chromatography

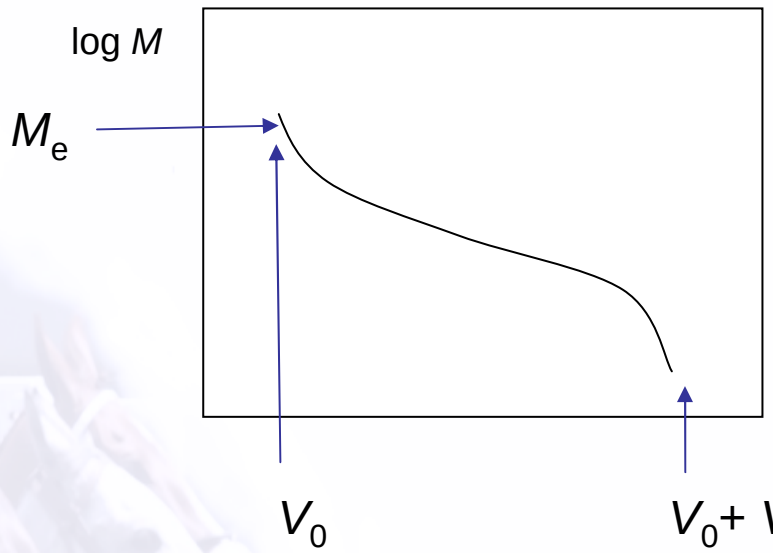


solvent flow

Partition between the flowing solvent and the solvent in the pores

Elution time (volume) is a function of the particle (hydrodynamic) size

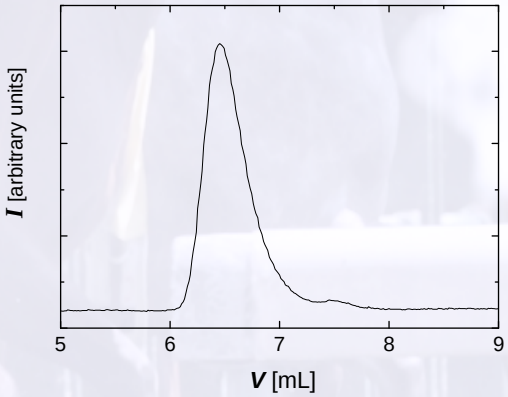
Above certain size all particles are equal, flow only through the interstitial volume



log M=a +b V +….

Detectors: (i) mass sensitive (refractometer, evaporative light scattering detection)
(ii) molecularly sensitive (end group UV absorption)
(iii) molecular-mass sensitive (light scattering, viscometric)

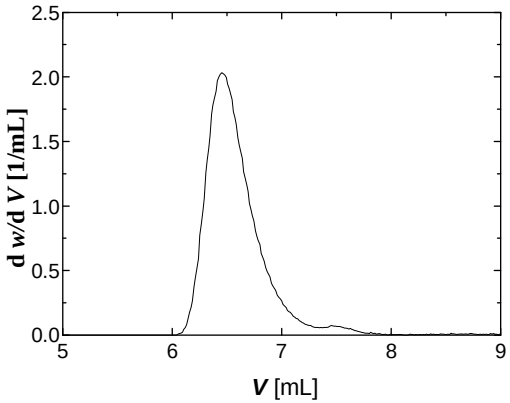
Standard configuration (i); up-to-date = multidetector (i)&(iii)



Baseline substraction

Normalization

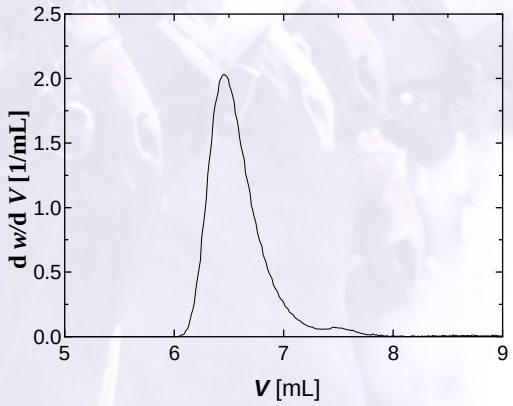
$$w(V) = \frac{I(V)}{\int_{V_L}^{V_R} I(V)\,\mathrm{d}V}$$

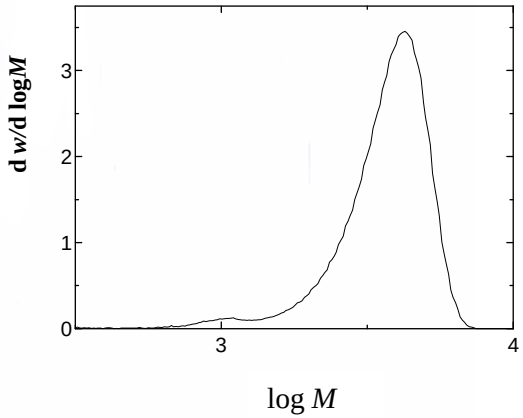


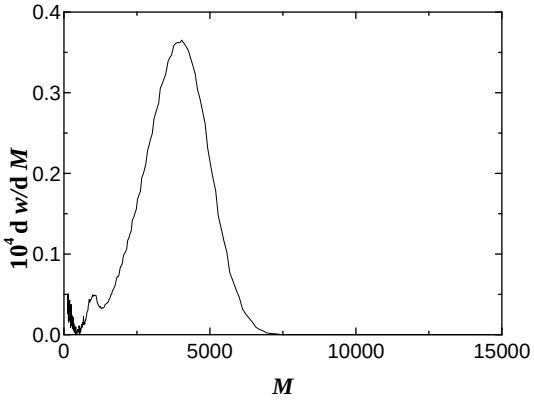
Point to point correspondence of cumulative *V* and M or log *M* distributions

$$\int_{\log M_L}^{\log M} w(\log M)\,\mathrm{d}\log M = \int_{V}^{V_L} w(V)\,\mathrm{d}V = \int_{\log M_L}^{\log M} w(V)\frac{\mathrm{d}V}{\mathrm{d}\log M}\,\mathrm{d}\log M$$

$$w(\log M) = \frac{-w(V)}{\frac{\mathrm{d}\log M}{\mathrm{d}V}} \qquad w(M) = \frac{w(\log M)}{2.303M}$$







$$\int_0^{\infty} \frac{\mathrm{d}w}{\mathrm{d}\log M}\,\mathrm{d}\log M = \int_0^{\infty} \frac{\mathrm{d}w}{\mathrm{d}M}\,\mathrm{d}M = 1$$

Mn = 3100 Mw = 3780 PI = 1.22

$M(V)$ – valid for the column, polymer, solvent etc

SEC with a mass detector only

- calibration by polymer standards
- universal calibration

– hydrodynamic volume $[\eta]M$ (V) Mark-Houwink Eq. $\log [\eta]M = \log K + (1+a)\log M$

- polystyrene calibration

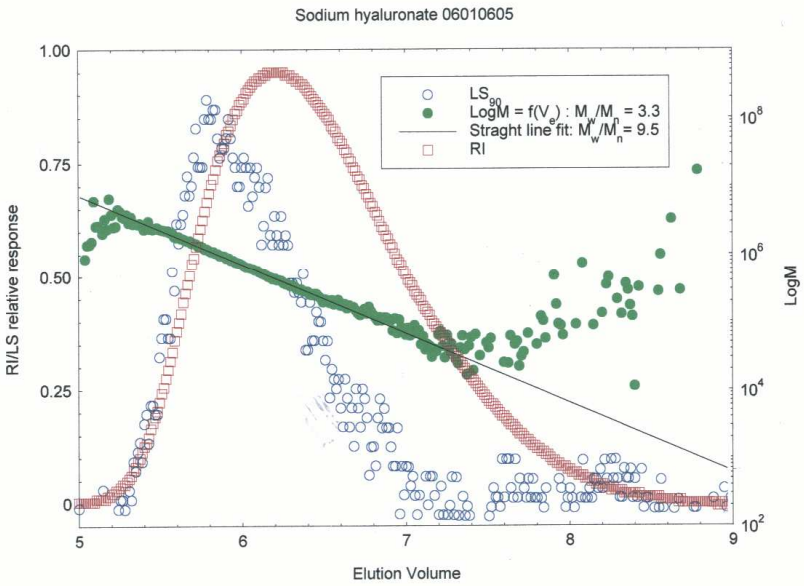
SEC with mass & molecular-mass detectors

viscosity detector – gives M through the universal calibration without Mark-Houwink parameters

static light-scattering detector

Averages of M:
directly according discreet definitions

Distribution: in two steps
(i) LS data are used for the calibration equation
(ii) RI data are treated in standard way

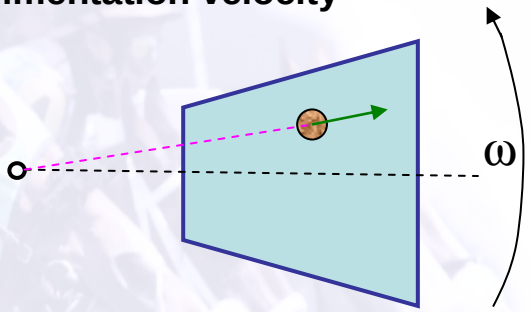


Sedimentation Analysis – Analytical Ultracentrifuge

(macromolecular archelogy? – Swedberg 1923, Nobel prize 1926)

Declared clinically dead in 1980's but then resurrected (natural macromolecules)

sedimentation velocity



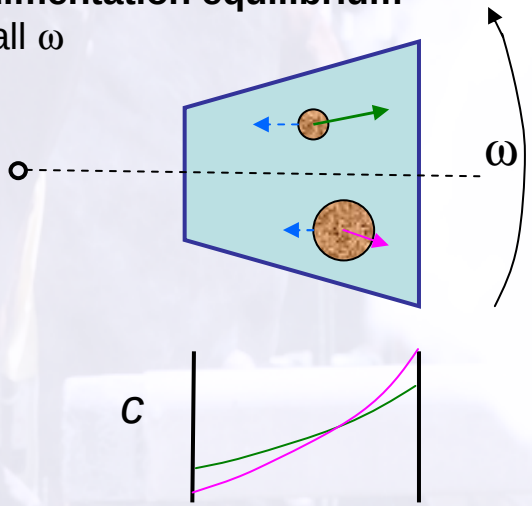
centrifugal force=friction resistance (*f u*) => sedimentation velocity *u*

sedimentation coefficient *s*

$$s = \frac{u}{\omega^2 r} = \frac{M(1-\bar{v}\rho)}{\mathrm{N_A} f} = \frac{MD(1-\bar{v}\rho)}{\mathrm{R}T}$$

sedimentation equilibrium

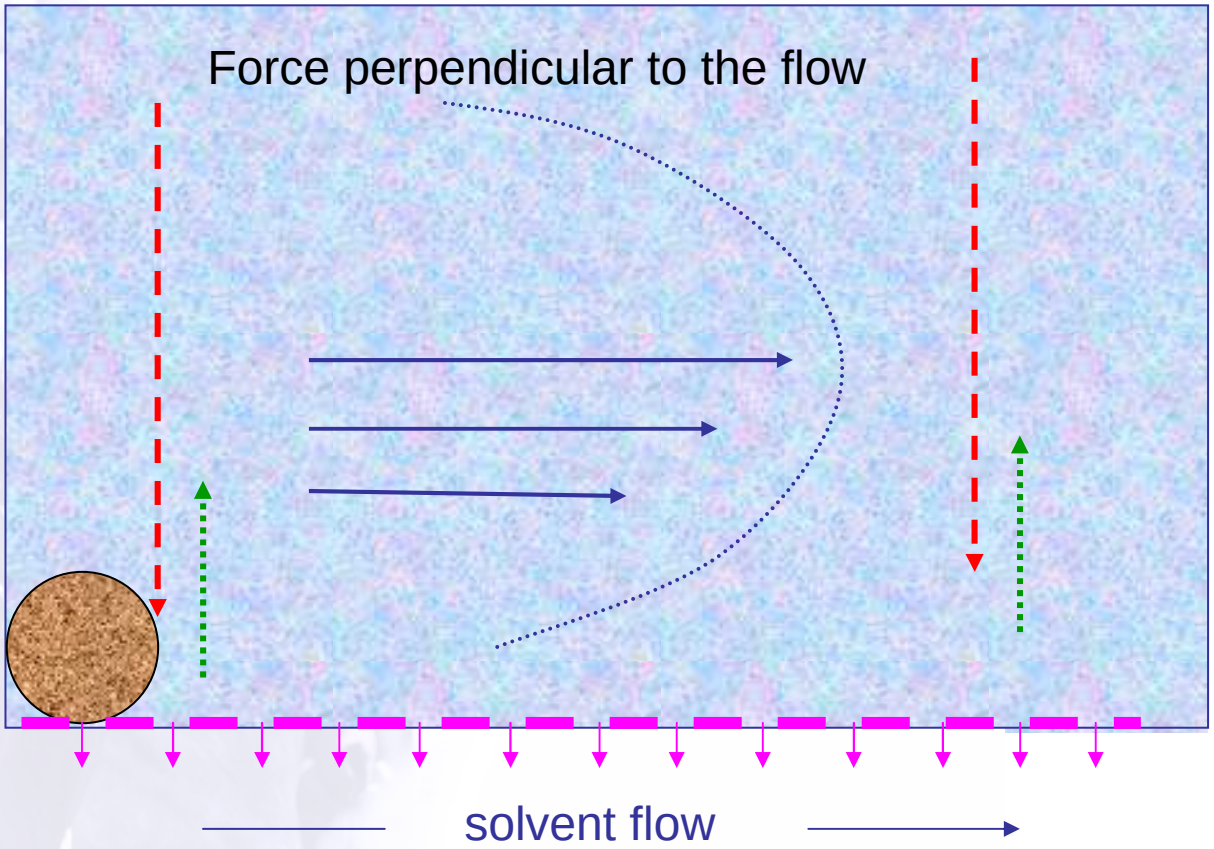
small ω



sedimentation creates temporal concentration gradient which is opposed by diffusion, equilibrium gradient is achieved

$$\frac{1}{r}\frac{\mathrm{d}c}{\mathrm{d}r} \sim M$$

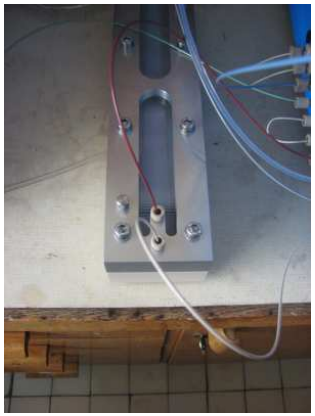
Principle of Field –Flow Fractionation
(J. C. Giddings)



field

thermal, electrical..

assymetrical flow



Elution time (volume) is a function of the particle (hydrodynamic) size
bigger particles (up to 0.1 mm vs. SEC <100 nm) smaller adsorption

change of mechanism (bigger particles first), absolute detection LS

Mass Spectrometry

Why MS if we have SEC? Resolution

MS: $M/w_{1/2}=10000$ SEC: $N_{tp}=5.54(V/w_{1/2})^2=10000$ $V/w_{1/2}=42$

The Nobel Prize in Chemistry 2002

"***for the development of soft desorption ionisation methods for mass spectrometric analyses of biological macromolecules***"

MALDI-TOF mass spectrometry

Mass spectrometry

Principle:
a charge particle is accelerated in electromagnetic field

In electric field $\frac{1}{2}mv^2 = zeU$

For measurement of molecular weight, *M*,

(i) the sample must be vaporized and charged (ion source)
(ii) particles must be separated according to *M*/*z* (mass analyzer)
(iii) particles with the same *M*/*z* must be counted (detector)

Low-molecular-weight compounds:

M is used for identification

vaporization puts an upper limit on measured *M*

the most widely used electron impact ionizations fragments the sample molecules

Fragmentation gives information on the structure of the compound

For a long time, polymer researches used MS only for analyzing

polymer additives

pyrolysis products

etc…

At the same time, they were fascinated by the MS precision

M atrix
A ssited
L aser
D esorption
I onization

T ime
O f
F light

M ass
S pectrometry

Matrix:
2,5-dihydroxybenzoic acid
1,8,9-trihydroxyantracene

Laser:
337 nm, pulse <4 ns, 40 kW/4mW

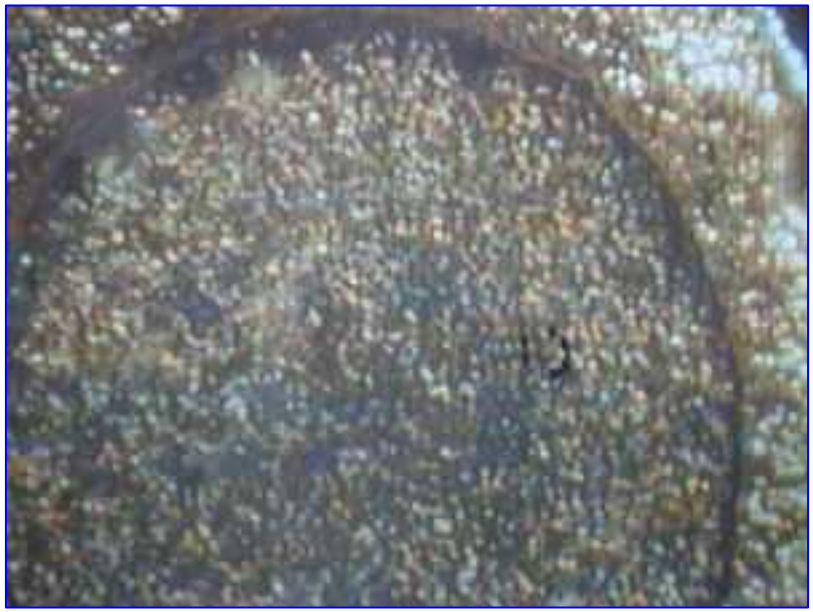
Sample preparation

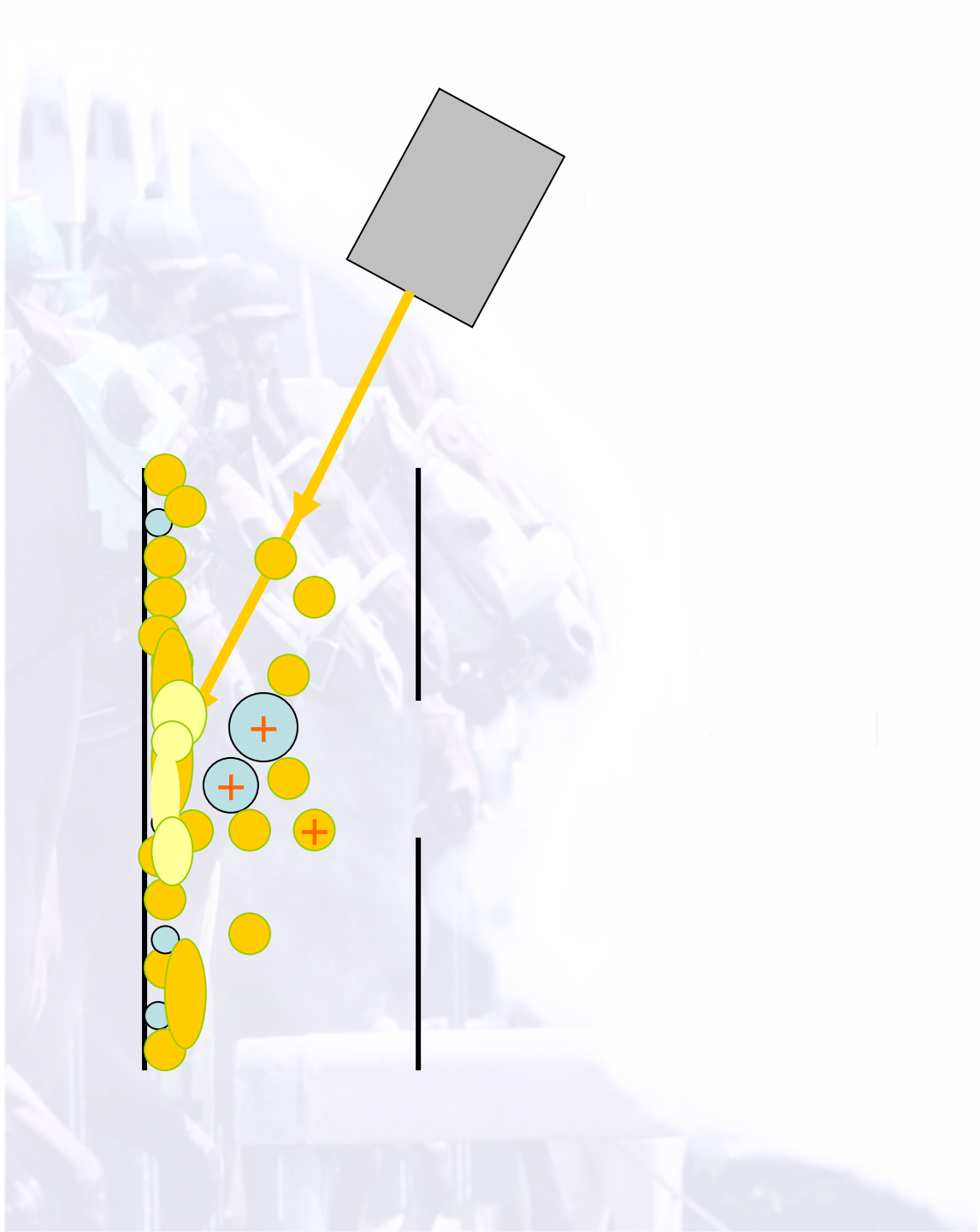
1- 2 µL per spot (2-10x)

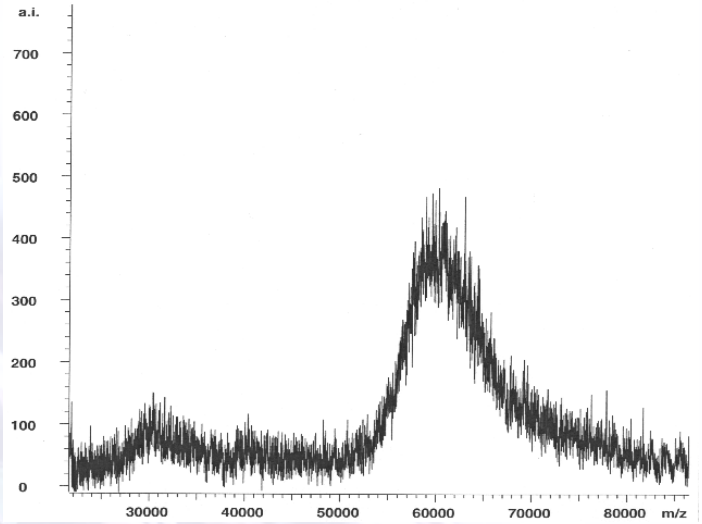
0.2% sample

1-2% matrix

& ionizitation agent (NaCl, AgTFA)



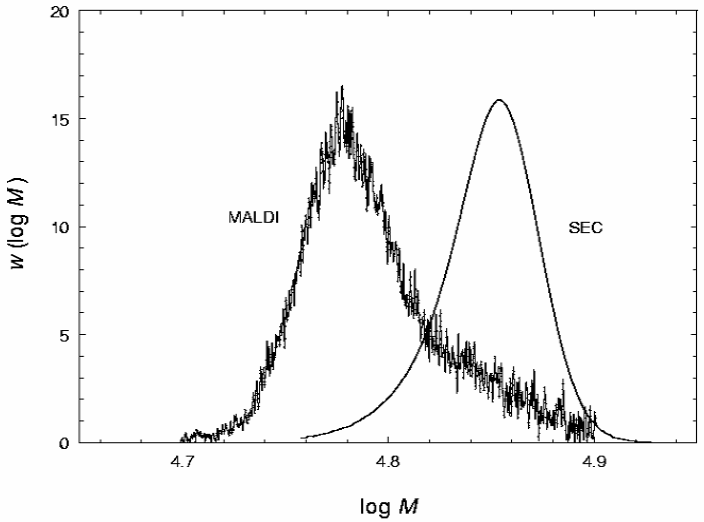




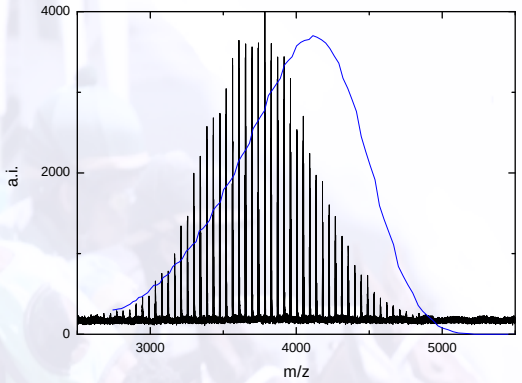
PST M_w/M_n(kDa)

MALDI 62.3/61.9

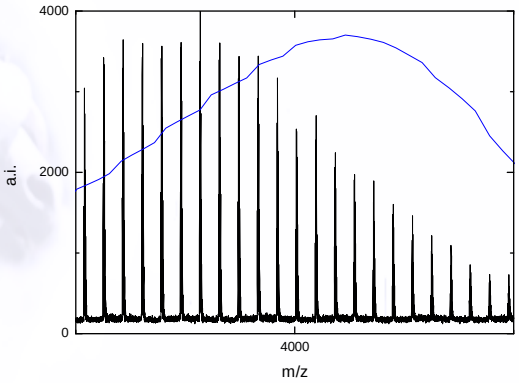
SEC 71.3/71.1



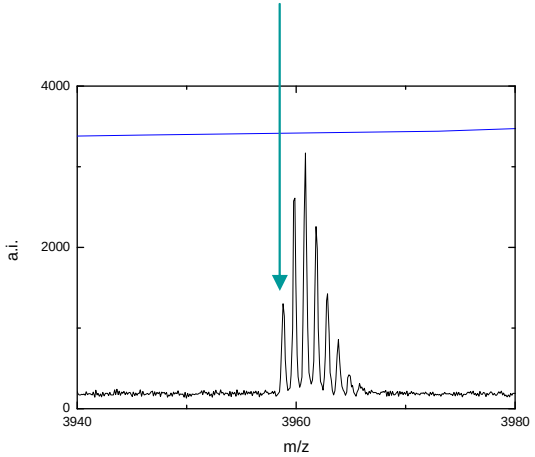
For samples with M>20 000 multidetector SEC is the first choice



MALDI-TOF MS can distinguish individual oligomers



Monoisotopic peak
(C^{12} only)



and even isotopic resolution
(in reflector mode)

The strength of MALDI-TOF is with samples M<20000

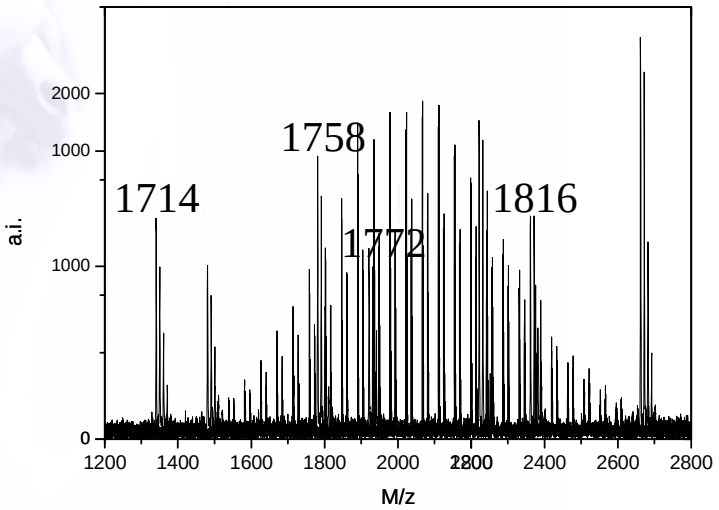
(For samples with M>20 000, the first choice is the multi-detector SEC)

$$M = M_{eg1} + n\,M_m + M_{eg2} + M_{ia}$$

$$HO\,[CH_2CH_2O]\,[CH_2CH_2O].....[CH_2CH_2O]\,H\;\;Na^+$$

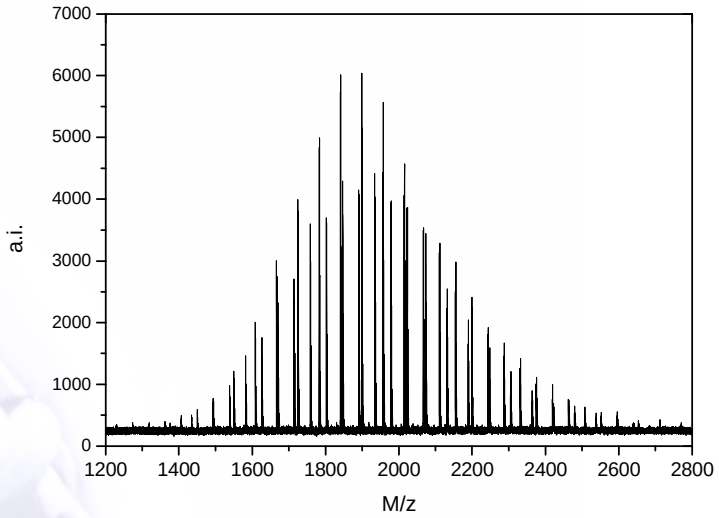
PEG:MPEG

1 : 1



17 + 39 * 44 + 1 + 23 = 1758

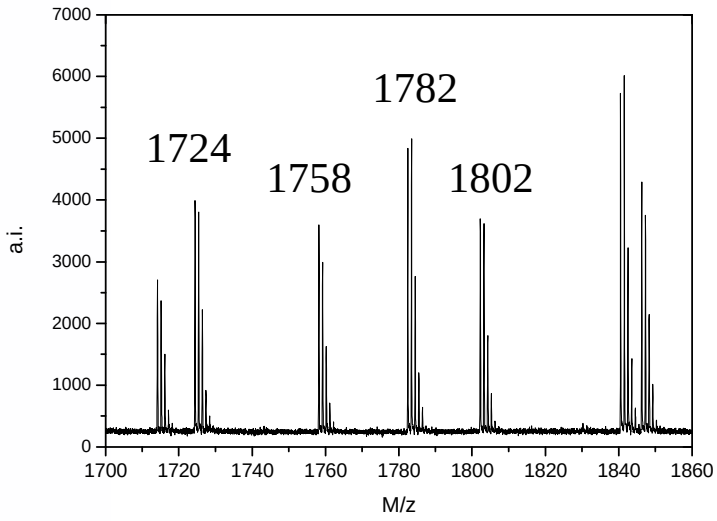
Mixture of two homopolymers



PEG:PPG

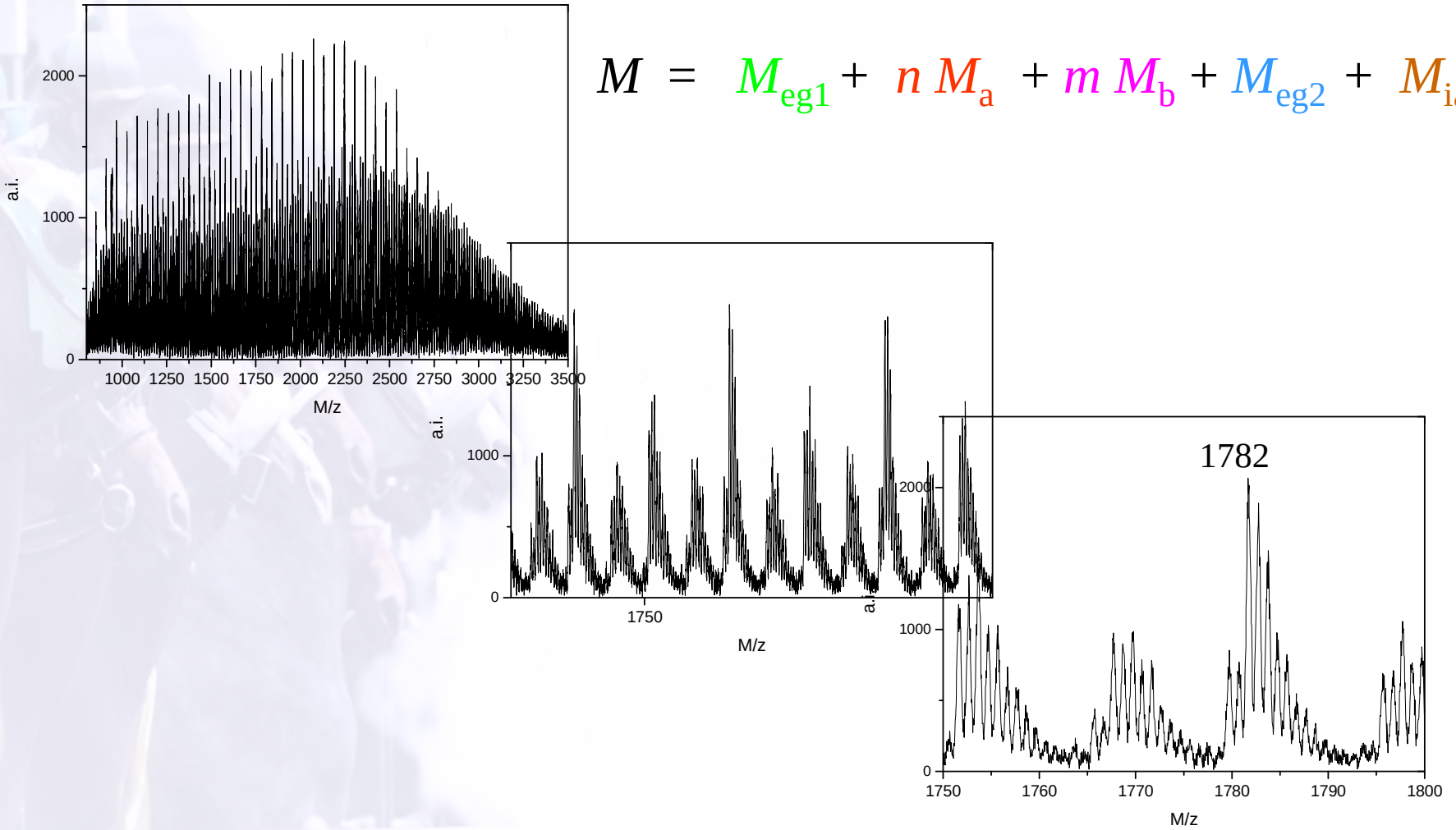
PEG : PPG

2 : 1



Binary copolymers (PEG/PPG -Pluronic)

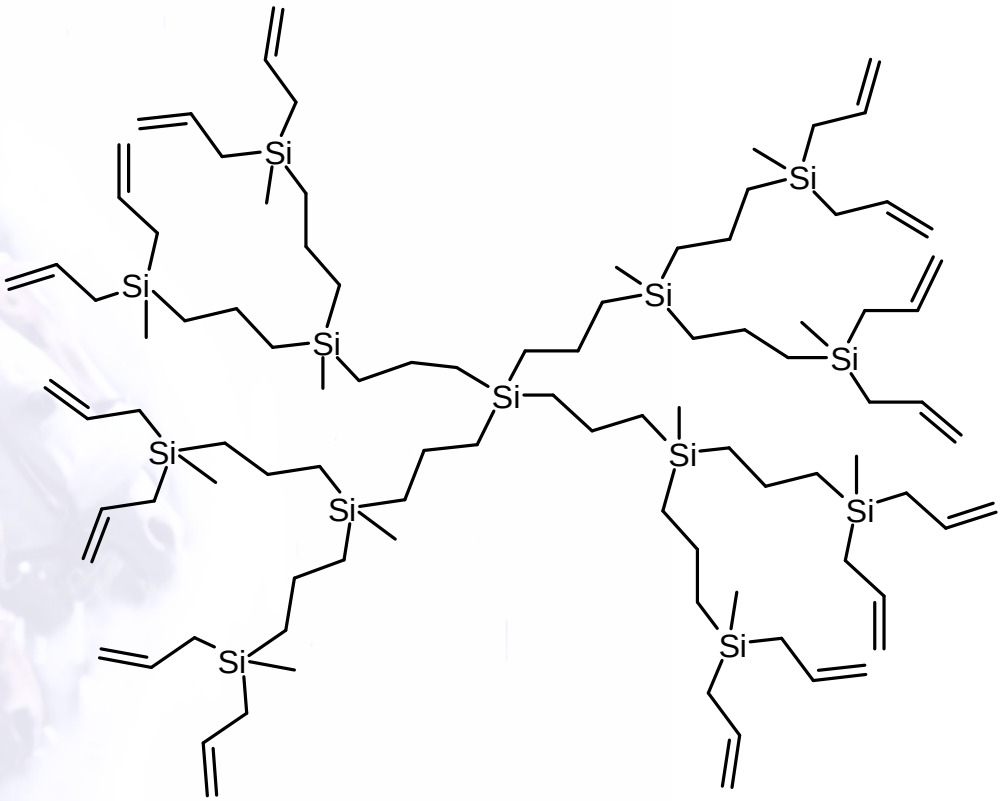
$$M = M_{eg1} + n M_a + m M_b + M_{eg2} + M_{ia}$$



1782=17+30*58+1+23

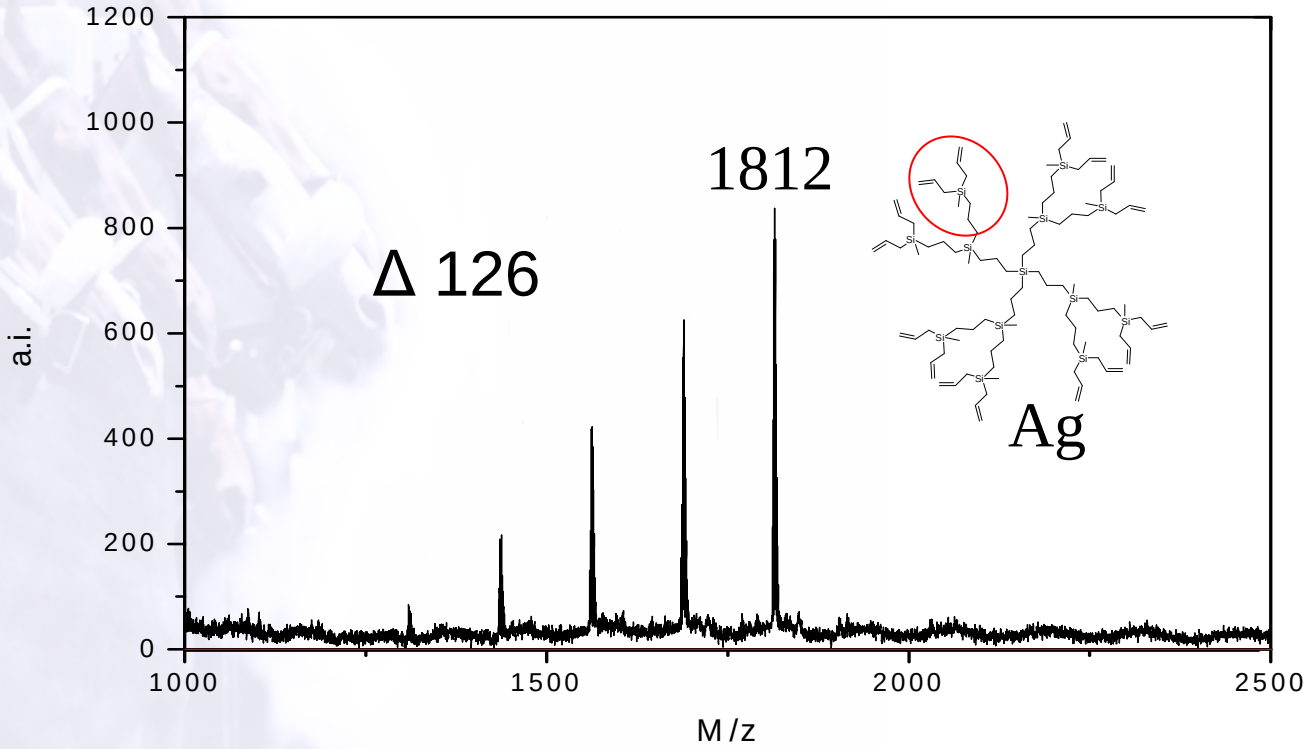
1782=17+29*44+8*58+1+23

22*58 = 29*44



dendrimer

MALDI-TOF mass spektrum of 2nd generatiom carbosilane dendrimer (defect detection)



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Lecture:

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