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Chapter 2: SYNTHESIS AND DISTRIBUTIONS

2.1 Distributions - Definitions

Distributions of molecular weights

- degree of polymerization N = number of monomers constituting the polymer
- molar mass $m = Nm_0$ with $m_0 =$ monomer molar mass
- mass of the polymer $M = m/N_A$ with $N_A =$ Avogadro number
- total mass $M = \sum_i M_i$
- total number $n = \sum_i n_i$

Polymerizations result in more or less broad distributions of molecular weights

- number fraction $$x_i = \frac{n_i(M_i)}{\sum_i n_i(M_i)} = \frac{n_i(M_i)}{n}$$
- weight fraction $$w_i = \frac{x_i M_i}{\sum_i x_i M_i} = x_i\left(M_i\right)\frac{M_i}{M_n}$$
- z-fraction $$z_i = w_i(M_i)\frac{M_i}{M_w}$$

Distributions can be characterized by directly measurable moments $\mu_k = \sum_i x_i M_i^k$

- number average $$M_n = \frac{\sum_i x_i M_i}{\sum_i x_i} = \sum_i x_i M_i = \mu_1/\mu_0 = \mu_1$$
- weight average $$M_w = \frac{\sum_i x_i M_i^2}{\sum_i x_i M_i} = \frac{\sum_i x_i M_i^2}{M_n} = \sum_i w_i M_i = \mu_2/\mu_1$$
- z-average $$M_z = \frac{\sum_i x_i M_i^3}{\sum_i x_i M_i^2} = \frac{\sum_i w_i M_i^2}{\sum_i w_i M_i} = \frac{\sum_i w_i M_i^2}{M_w} = \mu_3/\mu_2$$

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- “Uneinheitlichkeit” $u = \frac{\mu_2}{(\mu_1)^2} - 1 = \frac{M_w}{M_n} - 1$
- “polydispersity” $\frac{M_w}{M_n}$

e.g. a distribution of 1000 spheres:

number n_i	number fraction x_i	sphere mass M_i	x_iM_i	$x_iM_i^2$	$x_iM_i^3$
		[g]	[g]	[$10^2 g^2$]	[$10^4 g^3$]
900	0.9	100	90	90	90
50	0.05	500	25	125	625
50	0.05	2500	125	3125	78125
		moments	μ_1=240	μ_2=3340	μ_3=78840

number average $M_n = \mu_1 = 240$ g

weight average $M_w = \mu_2 / \mu_1 = 1392$ g

z-average $M_z = \mu_3 / \mu_2 = 2360$ g

"Uneinheitlichkeit" $u = \frac{\mu_2}{(\mu_1)^2} - 1 = \frac{M_w}{M_n} - 1 = 4.8$

⇒ higher moments put stronger weight on heavier spheres.
Small number fractions of heavy spheres lead to drastic differences between the averages.

Averages

$$M_\beta = \frac{\int_0^\infty x(M) M^\beta dM}{\int_0^\infty x(M) M^{\beta-1} dM}$$

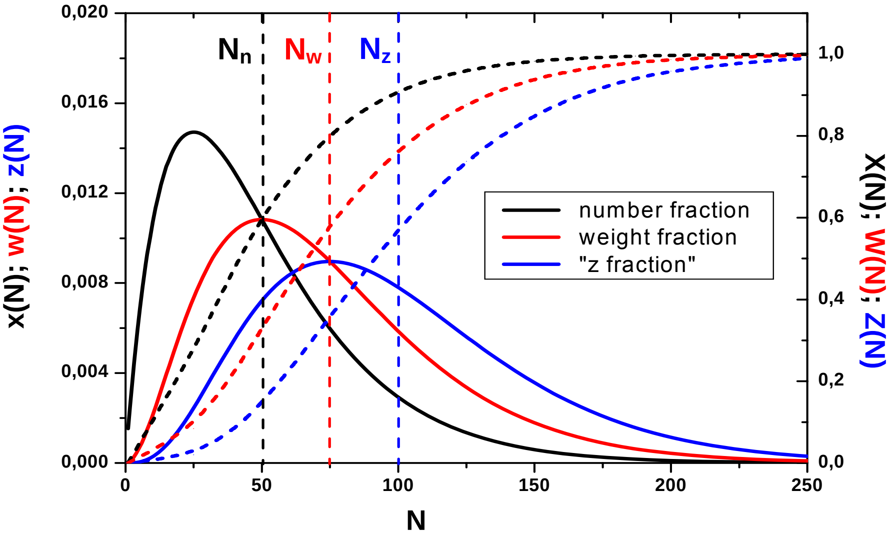
with β=1,2,3 for n,w,z-average $\int_0^\infty x(M)\, dM = 1$

averaging an arbitrary quantity A(M): $A_\beta = \dfrac{\int_0^\infty x(M) M^{\beta-1} A(M)\, dM}{\int_0^\infty x(M) M^{\beta-1} dM}$

Integral distributions X, W and Z yield the number average, mass average and z-average of a sample with M≤ M*, respectively: $X = \int_0^{M^*} x(M)\, dM$, $W = \int_0^{M^*} w(M)\, dM$ and $Z = \int_0^{M^*} z(M)\, dM$.

e.g. Schulz-Zimm distribution (k=2) (see radical polymerization)

N_n: N_W: N_Z=1: (3/2): 2



Kinetics

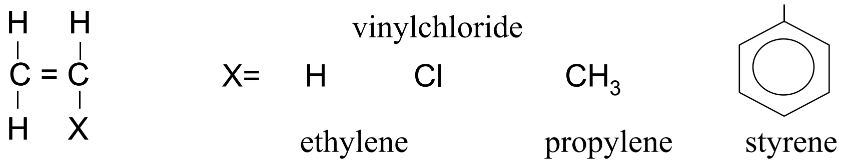
is the study of the speed at which chemical processes take place. In a chemical reaction it is the amount of product that forms or the amount of reactant that disappears in a given time interval and per unit volume.

Molecular weight distributions

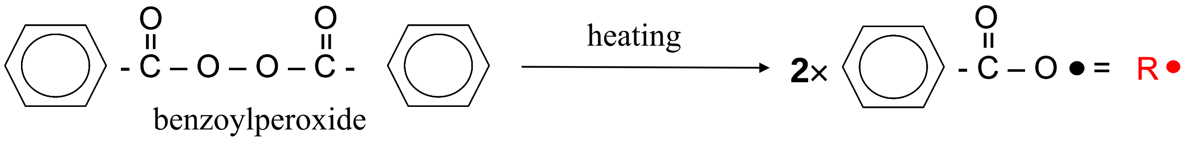
can be calculated from 1. the kinetics of elementary chain reactions (e.g. radical and ionic polymerization) and 2. from probability calculations (e.g. polycondensation). In the following the distributions are derived for different polymerization methods:

2.2 Radical polymerization

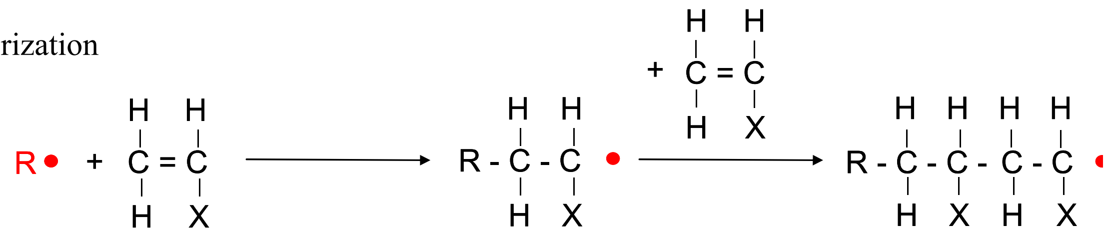
monomer



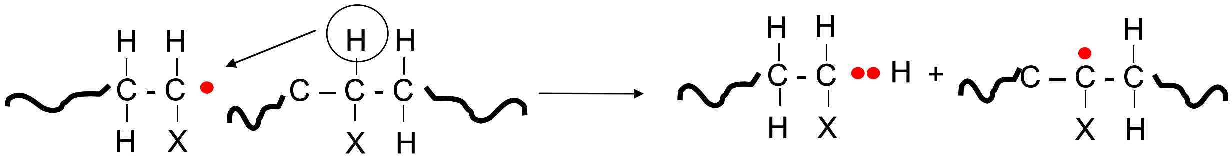
initiator



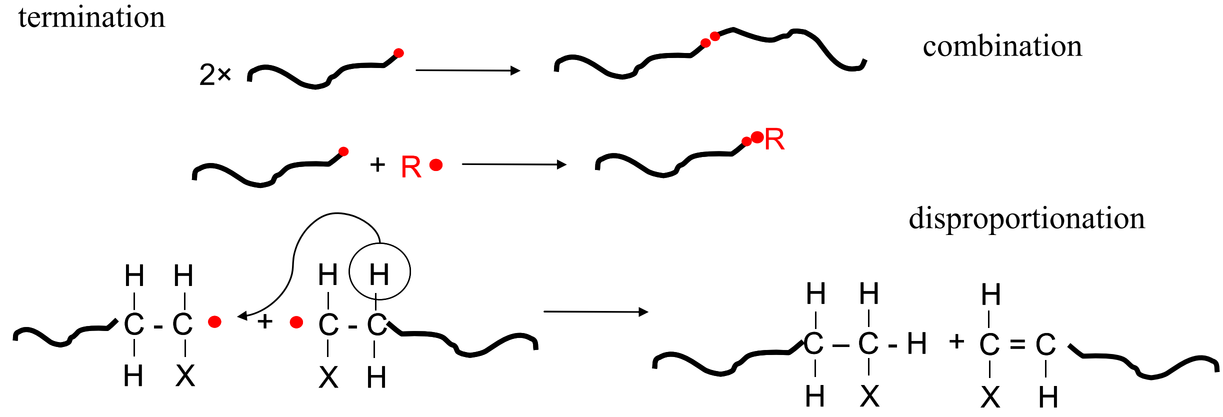
polymerization



chain transfer



termination



Kinetics: radical polymerization with combination termination

- radical generation $I \rightarrow 2R^*$ $$V_{start} = -\frac{d[I]}{dt} = k_1[I] = 2\frac{d[R^*]}{dt}$$
- termination $P_n^* + P_m^* \rightarrow P_{n+m}$ $$V_{term} = -\frac{d[P^*]}{dt} = k_2[P^*]^2$$
- stability condition $V_{start} = V_{term}$ $$k_1[I] = k_2[P^*]^2$$
- growth reaction $P_n^* + M \rightarrow P_{n+1}$ $$V_{Poly} = -\frac{d[M]}{dt} = k_3[P^*][M] = k_4[I]^{1/2}[M]$$

$\Rightarrow$ $[M](t) = [M]_0 \exp(-k_4[I]^{1/2}t)$ conversion $\dfrac{[M]_0 - [M]_t}{[M]_0} = 1 - \exp(-k_4[I]^{1/2}t)$

Derivation of the molecular weight distributions

Termination by combination of chains but without participation of a free radical

(A) generation of active monomers:

$$\frac{d[P_1^*]}{dt} = \underbrace{k\,[R][M]}_{\text{Monomer}} \underbrace{-k_p[P_1^*][M]}_{\text{Dimer}} \underbrace{-k_t[P_1^*][M^*] - k_t[P_1^*][P_2^*] - \ldots - k_t[P_1^*][P_x^*]}_{\text{Termination}}$$

(B) generation of active dimers:

$$\frac{d[P_2^*]}{dt} = \underbrace{k_p[P_1^*][M]}_{\text{Dimer}} \underbrace{-k_p[P_2^*][M]}_{\text{Trimer}} \underbrace{-k_t[P_2^*][P_1^*] - k_t[P_2^*][P_2^*] - \ldots - k_t[P_2^*][P_x^*]}_{\text{Termination}}$$

(C) generation of active x-mer:

$$\frac{d[P_x^*]}{dt} = k_p[P_{x-1}^*][M] - k_p[P_x^*][M]\left[-k_t[P_x^*][P_1^*] - k_t[P_x^*][P_2^*] - \ldots - k_t[P_x^*][P_x^*]\right]$$

- stationary state $$\frac{d[P_1^*]}{dt} = \frac{d[P_2^*]}{dt} = \ldots = \frac{d[P_x^*]}{dt} = 0$$
- rate of active monomer generation compensates all termination reactions
$$V_{ac} = k[R][M] = k_t[P^*]$$
where $[P^*]$= sum of all active chains and monomers
- [M] is (almost) constant for small conversions
$$0 = k[R][M] - k_p[P_1^*][M] - k_t[P_1^*][P^*]$$
$$\Leftrightarrow \quad V_{ac} = k[R][M] = k_p[P_1^*][M] + k_t[P_1^*][P^*]$$

$$\Rightarrow \quad \frac{V_{ac}}{[M]k_p} = [P_1^*]\left(1+\frac{[P^*]k_t}{[M]k_p}\right) = [P_1^*](1+\beta) \quad (*)$$

for all other equations analogous: $[P_{x-1}^*] = [P_x^*](1+\beta)$

$$\Rightarrow [P_x^*] = \frac{[P_{x-1}^*]}{(1+\beta)} = \ldots = \frac{[P_1^*]}{(1+\beta)^{x-1}} \overset{(*)}{=} \frac{V_{ac}}{[M]k_p}\frac{1}{(1+\beta)^x} \quad (**)$$

dead chains are produced by two active chains

$$\Rightarrow \quad \frac{d[P_x]}{dt} = k_t[P_x^*][P^*]$$

$$\Rightarrow \quad [P_x] = k_t[P_x^*][P^*]\cdot t + const \text{ with } const = [P_x]_{t=0} \equiv 0$$

$$\underset{(*)}{\overset{(**)}{\Rightarrow}} \quad [P_x] = k_t \underbrace{\frac{V_{ac}}{[M]\cdot k_p}\frac{1}{(1+\beta)^x}}_{=[P_x^*]} \underbrace{\frac{\beta k_p[M]}{k_t}}_{=[P^*]} \cdot t = \frac{V_{ac}\cdot\beta}{(1+\beta)^x}\cdot t \quad (\times)$$

- according to definition generates each activated monomer a polymer in the time t there are $V_{ac}\cdot t = \sum_x [P_x]$ active monomers ⇔ polymers generated

$$\overset{(\times)}{\Rightarrow} \quad x(N) = \frac{[P_N]}{\sum_N [P_N]} = \frac{\beta}{(1+\beta)^N}$$ **number fraction distribution**

$$\Rightarrow \quad N_n = \frac{\sum_N X(N)\cdot N}{\sum_N X(N)} = \frac{1+\beta}{\beta}$$ **averages**

$$N_w = \frac{\sum_N X(N)\cdot N^2}{\sum_N X(N)\cdot N} = \frac{\beta+2}{\beta}$$

$$N_z = \frac{\sum_N X(N)\cdot N^3}{\sum_N X(N)\cdot N^2} = \frac{\beta^2+6\beta+6}{(\beta+2)\beta}$$

$$\Rightarrow \quad w(N) = \frac{X(N)\cdot N}{N_n} = \frac{\beta^2 N}{(1+\beta)^{N+1}}$$ **weight fraction distribution**

for low radical concentrations (β<<1): $\Rightarrow N_n = \frac{1}{\beta}$; $N_w = \frac{2}{\beta}$; $N_z = \frac{3}{\beta}$

$$\Rightarrow N_n : N_w : N_z = 1:2:3$$

$$\Rightarrow \quad \frac{N_w}{N_n} = 2 \qquad \textbf{polydisperity}$$

$$\Rightarrow \quad u = \frac{N_w}{N_n} - 1 = 1 \qquad \textbf{“Uneinheitlichkeit”}$$

More general derivation leads to **Schulz-Zimm distribution**

- constant number of chains growth by random monomer addition until termination
- start of chain growth not necessarily at the same time
- concentration of active centers stays constant (stationarity condition)

$$x(N) = \frac{\beta^k N^{k-1} \exp(-\beta N)}{\Gamma(k)} \text{ with } \beta = \frac{k}{N_n}$$

$$\Rightarrow \quad w(N) = x(N) \frac{N}{N_n} = \frac{\beta^k N^k \exp(-\beta N)}{\Gamma(k) \cdot N_n} \qquad \textit{(typos in Elias)}$$

k = degree of coupling = number of chain combined to dead chain in termination reaction

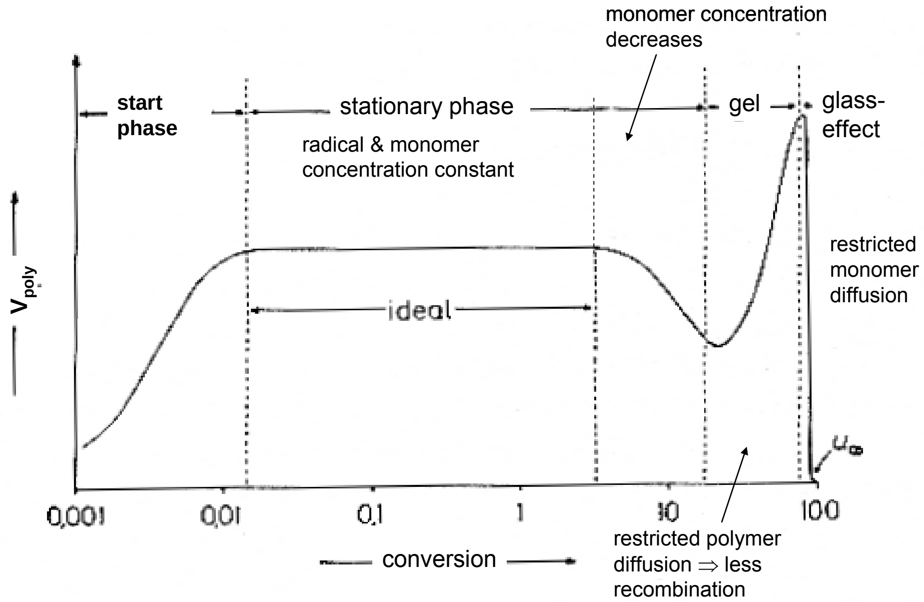
$$N_n = \frac{k}{\beta} \Rightarrow \frac{N_n}{k} = \frac{N_w}{k+1} = \frac{N_z}{k+2} \quad \text{(use integral definition)}$$

for k=1 $\qquad N_n = \frac{1}{\beta} \Rightarrow N_n : N_w : N_z = 1:2:3 \qquad$ (disproportionation)

for k=2 $\qquad N_n = \frac{2}{\beta} \Rightarrow N_n : N_w : N_z = 1:\frac{3}{2}:2 \qquad$ (combination of two chains)

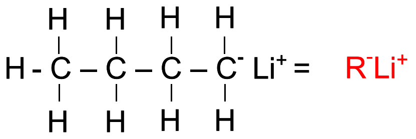
$$\Rightarrow \quad z(N) = w(N) \frac{N}{N_w} = w(N) \frac{N}{N_n} \frac{k}{k+1} \text{ with } N_w = \left(\frac{k+1}{k} \right) N_n$$

for radical polymerization with combination termination:



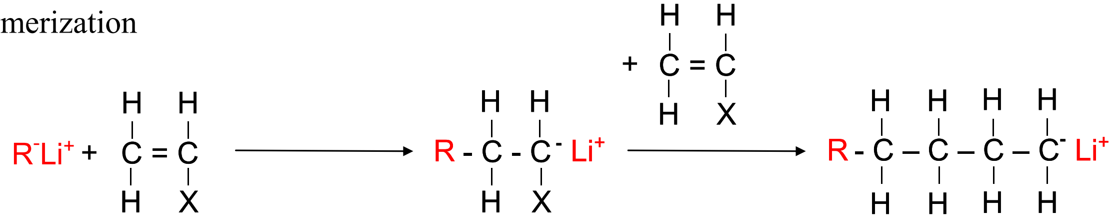
2.3 (An)ionic polymerization

initiator



$$\mathrm{H{-}CH_2{-}CH_2{-}CH_2{-}CH_2^-\,Li^+ = R^-Li^+}$$

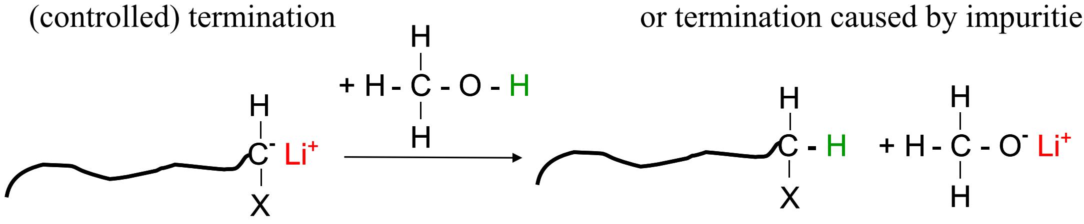
polymerization



$$\mathrm{R^-Li^+ + CH_2{=}CHX \longrightarrow R{-}CH_2{-}CHX^-\,Li^+ \xrightarrow{+\ CH_2=CHX} R{-}CH_2{-}CH_2{-}CH_2{-}CH_2^-\,Li^+}$$

(controlled) termination

or termination caused by impurities



$$\mathrm{\sim\!CHX^-\,Li^+ + H{-}CH_2{-}O{-}H \longrightarrow \sim\!CHX{-}H + H{-}CH_2{-}O^-\,Li^+}$$

Kinetics: (an)ionic polymerization

- no termination reaction
- concentration of active centers stays constant [P*]=constant
- all chains start to growth at the same time; instantanously at t=0

growth reaction $P_n^*+M \rightarrow P_{n+1}$ $V_{Poly} = -\frac{d[M]}{dt} = k_p[P^*][M]$

$\Rightarrow [M](t)=[M]_0\exp(-k_p[P^*]t)$ conversion $u = \frac{[M]_0-[M]_t}{[M]_0} = 1-\exp(-k_p[P^*]t)$

Derivation of the molecular weight distributions

initiator ions are instantanously converted to monomer ions

$\Rightarrow$ number of initiator ions $[I]=[P_1^*]_{t=0}$ number of monomer ions

monomer $$\frac{d[P_1^*]}{dt} = -k_p\underset{1\longrightarrow 2}{[M][P_1^*]}$$

dimer $$\frac{d[P_2^*]}{dt} = -k_p\underset{1\longrightarrow 2}{[M][P_1^*]} - k_p\underset{2\longrightarrow 3}{[M][P_2^*]}$$

x-mer $$\frac{d[P_x*]}{dt} = -k_p \underset{(x-1)\longrightarrow x}{[M][P_{x-1}*]} - k_p \underset{x\longrightarrow(x+1)}{[M][P_x*]}$$

reduction of monomer number is determined by the number of active centers
$$\frac{d[M]}{dt} = -k_p[M][P*] \text{ with } [P*] = \sum\nolimits_i [P_i*] = [I] = [P_1*]_{t=0} = const$$
$$= \text{number of growing chains}$$

define: $\nu = \frac{[M]_{t=0} - [M]}{[P*]} - 1 = N_n - 1$

ν gives us the number of monomers attached to one monoion P*
$$\frac{d\nu}{dt} = -\frac{d[M]}{dt}\frac{1}{[P*]} = k_p[M] \Leftrightarrow dt = \frac{1}{k_p[M]}d\nu$$

⇨ <u>coupled differential equation system</u>

monomer: $d[P_1*] = -k_p[P_1*]d\nu$
dimer: $d[P_2*] = [P_1*]d\nu - [P_2*]d\nu$
.
:
x-mer: $d[P_x*] = [P_{x-1}*]d\nu - [P_x*]d\nu$

(1) solution monomer: $[P_1*] = C\exp(-\nu)$ with $[\mathrm{P}_1*]_{t=0} = [P*] = [P_1*]_{\nu=0}$

$\Rightarrow [P_1*] = [P*]\exp(-\nu)$

(2) solution dimer: $d[P_2*] = [P*]\exp(-\nu)\,d\nu - [P_2*]d\nu$

solved by general solution of homogenous differential equation + special solution of inhomogeneous differential equation

hom. solution: $[P_2*]_h = C_1\exp(-\nu)$
inhom. solution: ansatz variation of constant $[P_2*]_i = C(\nu)\exp(-\nu)$

$$\Rightarrow \frac{d[P_2*]}{d\nu} = \frac{dC(\nu)}{d\nu}\exp(-\nu) - C(\nu)\exp(-\nu) = [P*]\exp(-\nu) - C(\nu)\exp(-\nu)$$
$$\Rightarrow \frac{dC(\nu)}{d\nu} = [P*] \Rightarrow C(\nu) = [P*]\cdot\nu + C_2$$

$\Rightarrow$ general solution $[P_2*] = [P_2*]_h + [P_2*]_i = ([P*]\nu + C)\exp(-\nu)$ with
$[P_2*]_{t=0} = 0 = [P_2*]_{\nu=0}$

$\Rightarrow [P_2*] = [P*]\cdot\nu\cdot\exp(-\nu)$

(3) solution trimer: $[P_3*]=\dfrac{\nu^2[P*]\exp(-\nu)}{2!}$

by induction method => for the (x-1)mer: $[P_{x-1}*]=\dfrac{\nu^{x-2}[P*]\exp(-\nu)}{(x-2)!}$

to solve the xth differential equation: $\dfrac{d[P_x*]}{dx}=\dfrac{\nu^{x-2}[P*]\exp(-\nu)}{(x-2)!}d\nu-[P_x*]$

general hom. solution: $[P_x*]_h=C_1\exp(-\nu)$

special inhom. solution: $[P_x*]_i=C(\nu)\exp(-\nu)$

$$\Rightarrow\frac{dC(\nu)}{d\nu}=\frac{\nu^{x-2}[P*]}{(x-2)!}\Rightarrow C(\nu)=\frac{\nu^{x-1}[P*]}{(x-1)!}+C_2\quad\text{with }[P_x*]_{t=0}=0=[P_x*]_{\nu=0}$$

$$\Rightarrow[P_x*]=\frac{\nu^{x-1}[P*]}{(x-1)!}\exp(-\nu)$$ _general solution

⇒ number fraction of polymers with degree of polymerization N:

$$\Rightarrow x(N)=\frac{[P_N*]}{[P*]}=\frac{\nu^{N-1}\exp(-\nu)}{(N-1)!}\quad\text{with}\quad\nu=N_n-1$$ **Poisson distribution**

$$\Rightarrow\quad N_n=\sum_{N=1}^{\infty}x(N)N=\nu+1=N_n$$ **averages**

$$N_w=\frac{\sum_{N=1}^{\infty}x(N)N^2}{\sum_{N=1}^{\infty}x(N)N}=\frac{\nu^2+3\nu+1}{1+\nu}=\frac{N_n{}^2+N_n-1}{N_n}=N_n+1-\frac{1}{N_n}$$

$$N_z=\frac{\sum_{N=1}^{\infty}x(N)N^3}{\sum_{N=1}^{\infty}x(N)N^2}=\frac{1+7\nu+6\nu^2+\nu^3}{1+3\nu+\nu^2}=\frac{N_n{}^3+3N_n{}^2-2N_n-1}{N_n{}^2+N_n-1}$$

polydispersity: $\dfrac{N_w}{N_n}=\dfrac{N_n+1}{N_n}=1+\dfrac{(N_n-1)}{N_n{}^2}\overset{\text{for large }N_n}{\approx}1+\dfrac{1}{N_n}$

“Uneinheitlichkeit” $u=\dfrac{N_n-1}{N_n{}^2}\approx\dfrac{1}{N_n}$

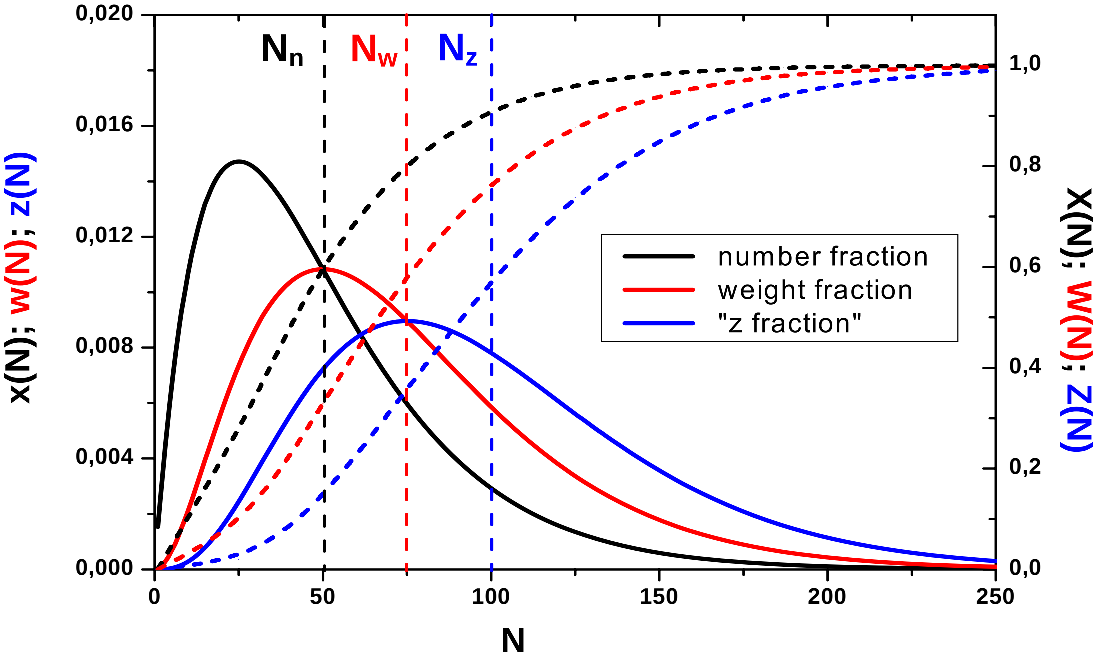
weight fraction distribution $w(N)=x(N)\dfrac{N}{N_n}=x(N)\dfrac{N}{\nu+1}=\dfrac{N\cdot\nu^{N-1}\exp(-\nu)}{(N-1)!\,(\nu+1)}$

Comparison distributions ionic and radical polymerization

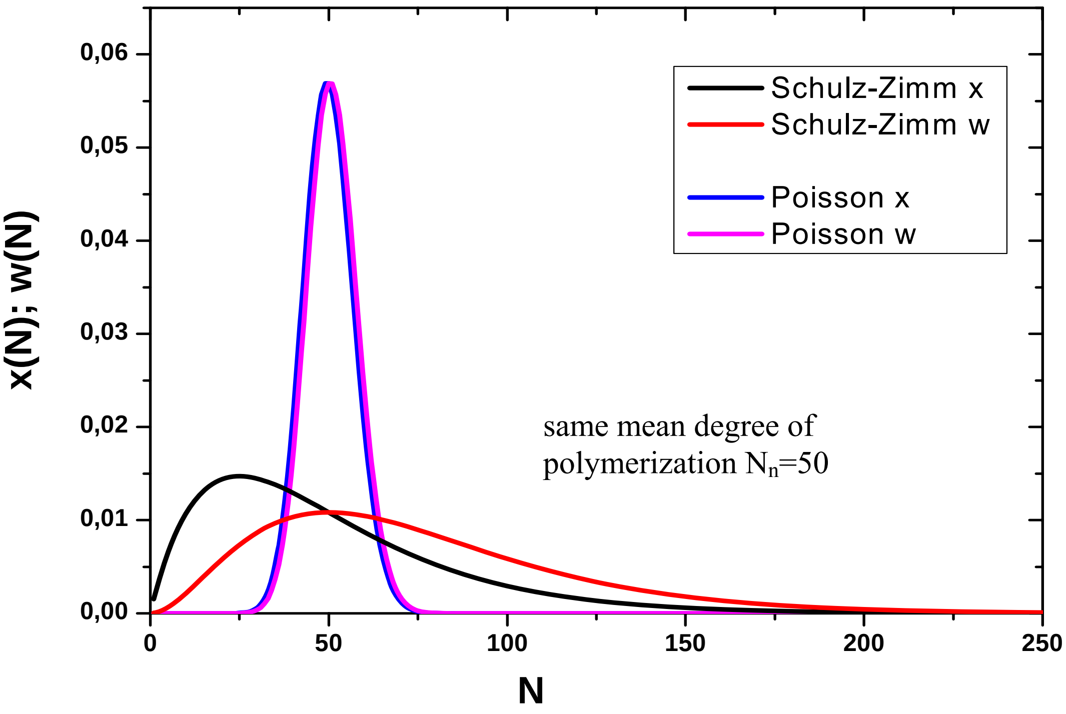
Schulz-Zimm (k=2) $N_n : N_w : N_z = 1 : (3/2) : 2$

Poisson $N_w : N_n = 1 + N_n^{-1}$

Schulz-Zimm distribution



Schulz-Zimm (k=2) and Poisson distribution



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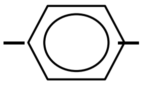
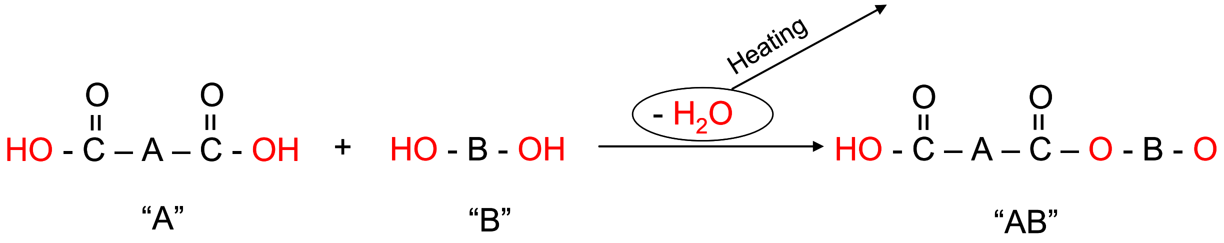
2.3 Polycondensation

e.g. polyester

A = di-acid = adipic acid, terephthalic acid

$-(CH_2)_4-$;


B = di-alcohol = ethylene glycol; butanediol $-(CH_2)_2-$; $-(CH_2)_4-$



- chain growth reaction: $(AB)_x + A$ $B + (AB)_x$ $(AB)_x + (AB)_y$
- stoichiometric ratio of acid/alcohol has strong impact on the final molecular weight
- termination**:** chain closure, monofunctional impurities

Kinetics: polycondensation

A = di-acid; B = di-alcohol

- no termination reaction
- acid acts as catalyst [A]=[C]
- [A]=[B]

"AB" growth reaction

$$V_{Poly} = -\frac{d[A]}{dt} = k[C][A][B] = k[A]^3$$

$$\Leftrightarrow \frac{1}{[A](t)^2} = 2kt + \frac{1}{[A]_0^2}$$

$$\Leftrightarrow \frac{[A]_0^2}{[A](t)^2} - 1 = [A]_0^2 2kt$$

$$\Leftrightarrow [A](t) = \frac{1}{\sqrt{2kt + [A]_0^{-2}}}$$

conversion

$$u = 1 - \frac{1}{\sqrt{2kt[A]_0^2 + 1}}$$

- no side reactions, i.e. no termination
- A and B are bifunctional

number of functional group A at t=0: n_A^0
B at t=0: n_B^0

define $r_0 = \left(\frac{n_A^0}{n_B^0} \right) \leq 1$ (stoichiometric ratio)

p_A ; p_B with $p_{A/B}$ =fraction of reacted A & B groups, respectively number of monomer units:

$$n_M = \frac{n_A^0 + n_B^0}{2} = \frac{n_A^0}{2}[1 + r_0]$$

number of functional groups after time t:

$$n_A = n_A^0 - p_A n_A^0 \quad \text{and} \quad n_B = n_B^0 - p_B n_B^0 = n_B^0 - p_A n_A^0$$

total $n_E = n_A + n_B = n_A^0(1 - 2p_A) + n_B^0 = n_A^0(1 - 2p_A) + n_A^0 \cdot r_0^{-1} = n_A^0(1 - 2p_A + r_0^{-1})$

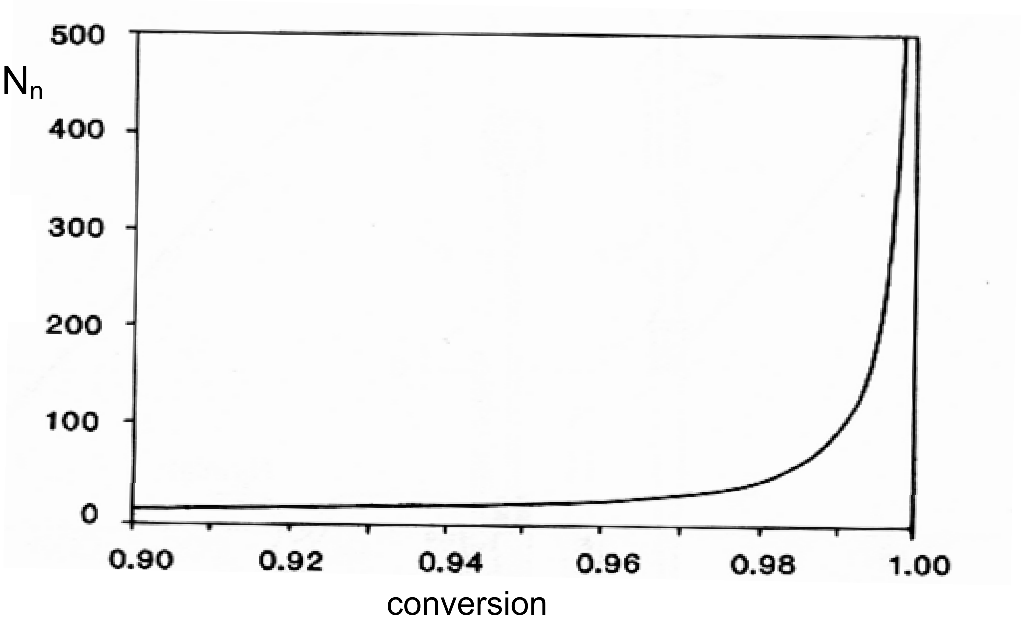
$\Rightarrow N_n = 2\frac{n_N}{n_E}$ (bifunctional groups)

$$\Leftrightarrow N_n = \frac{(1 + r_0^{-1})}{(1 - 2p_A + r_0^{-1})} = \frac{r_0 + 1}{1 + r_0 - 2p_A \cdot r_0}$$

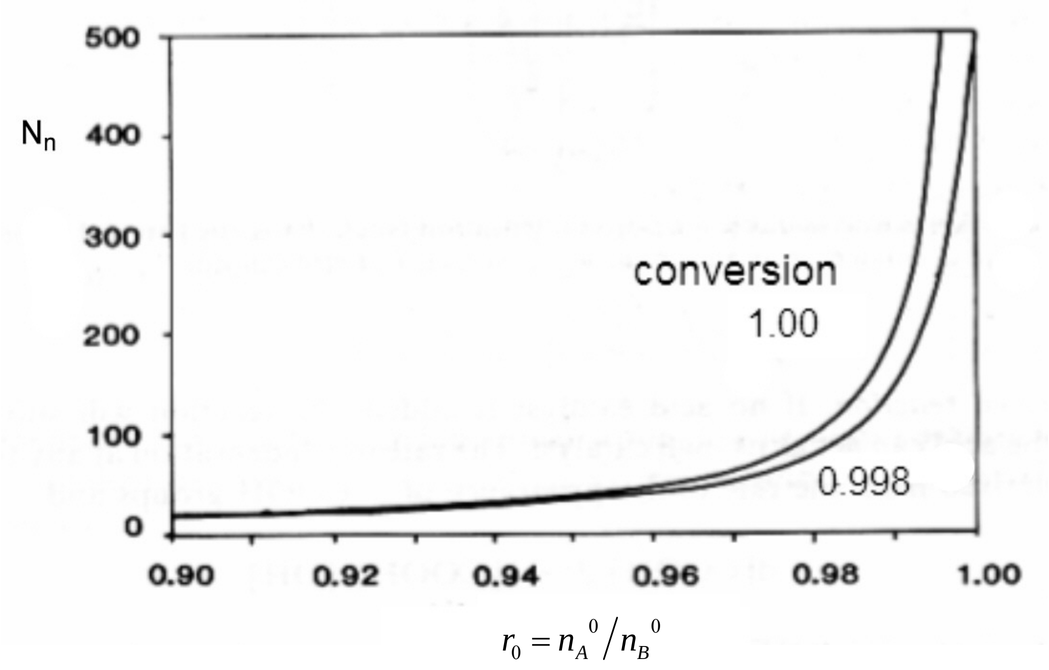
limits

- for $r_0=1$ and $p_A=1$ $\Rightarrow N_n = \infty$ (one long chain)
- for $r_0<1$ and $p_A=1$ $\Rightarrow N_n = \frac{1 + r_0}{1 - r_0}$ $r_0=0.99$ $\Rightarrow$ $N_n=199$
- for $r_0=1$ and $p_A>1$ $\Rightarrow N_n = \frac{1}{1 - p_A}$ $p_A=0.99$ $\Rightarrow$ $N_n=100$
- for $r_0=1$ ABABAB A and B ends with same probability
  $r_0<1$ BABAB same ends with excess component

N_n as a function of conversion



N_n as a function of the stoichiometric ratio $r_0 = n_A^0 / n_B^0$



Derivation of molecular weight distributions

Derivation not from kinetics but by probability treatment

- $r_0=1$
- all functional groups have the same reaction probability

p = conversion of reaction
p-1 = fraction of non reacted groups

(1)	dimer is build with the probability	p
(2)	trimer	p^2
(3)	tetramer	p^3
.		
:		
(x)	x-mer	p^{x-1}

⇒ the probability to find a polymer with N monomers $p_N = \underbrace{(p^{N-1})}_{\text{probability to find a (N-1)mer}} \quad \underbrace{(1-p)}_{\text{probability to find a monomer}}$

$$x(N) = \frac{N_{total} \times p_N}{N_{total}} = p^{N-1}(1-p)$$ **number fraction distribution**

$$w(N) = x(N) \cdot \frac{N}{N_n} = p^{N-1}(1-p)\frac{N}{N_n}$$ **weight fraction distribution**

$$\Rightarrow \quad N_n = \sum_{N=1}^{\infty} x(N)N = \frac{1}{1-p}$$ **averages**

$$N_w = \frac{\sum_{N=1}^{\infty} x(N)N^2}{\sum_{N=1}^{\infty} x(N)N} = \frac{1+p}{1-p}$$

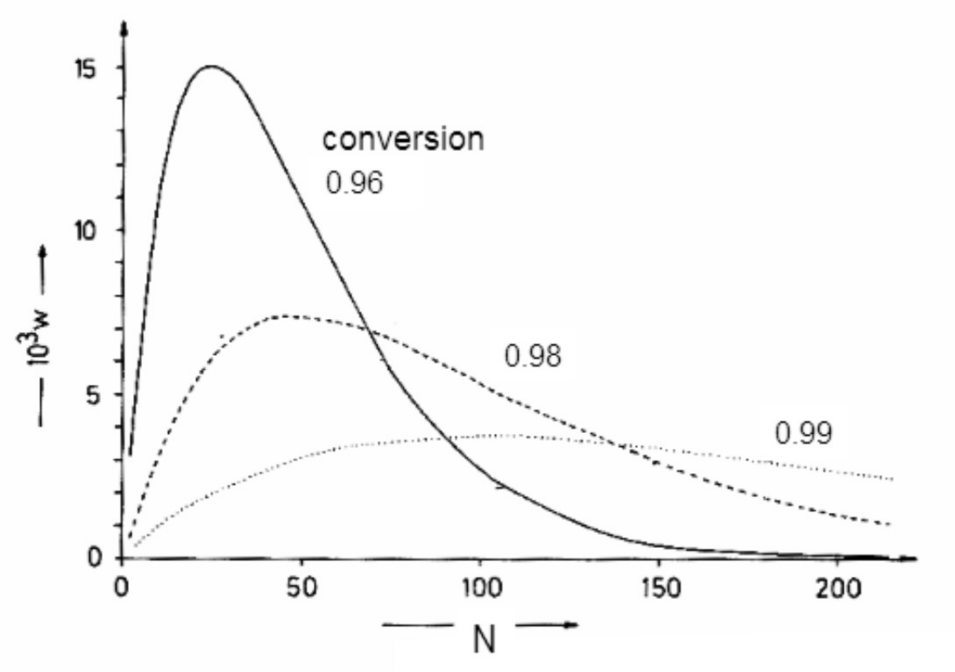
$$N_z = \frac{\sum_{N=1}^{\infty} x(N)N^3}{\sum_{N=1}^{\infty} x(N)N^2} = \frac{p^2+4p+1}{1-p^2}$$

polydispersity $$\frac{N_w}{N_n} = p+1$$

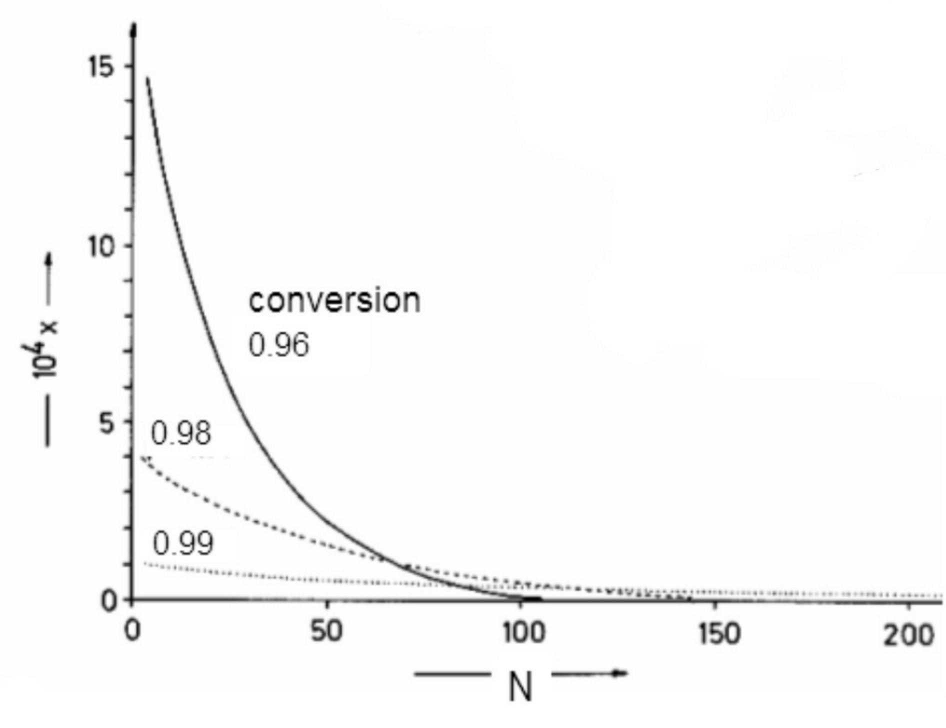
“Uneinheitlichkeit” $$u = \frac{N_n}{N_w} - 1 = p$$

weight fraction distribution $$w(N) = p^{N-1}(1-p)\frac{N}{N_n} = p^{N-1}(1-p)^2 N$$

weight fraction distribution



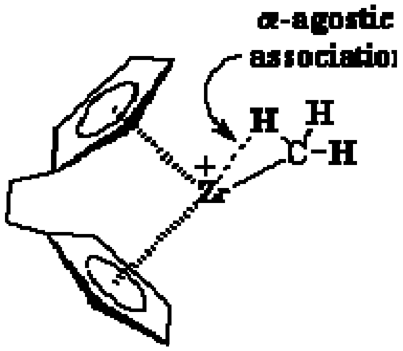
number fraction distribution



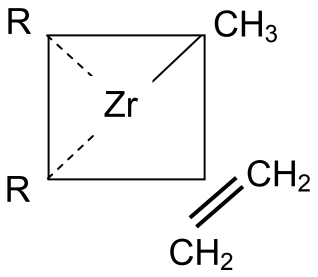
2.4 Metallocene catalysts

Positively charged metal ion sandwiched between to negatively charged cyclopentadienyl anions

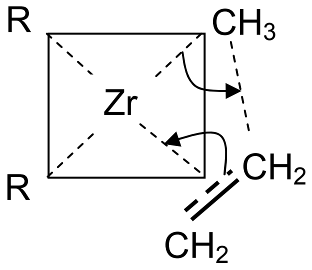
empty site at the Zr complex is occupied by dative bonded ethylene.



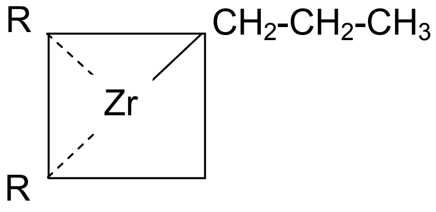
complexation with a monomer



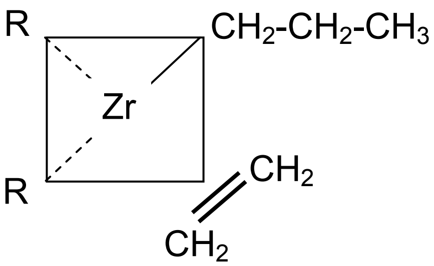
destabilization of double bond



insertion of ethylene



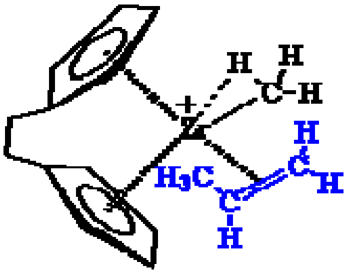
complexation with a monomer



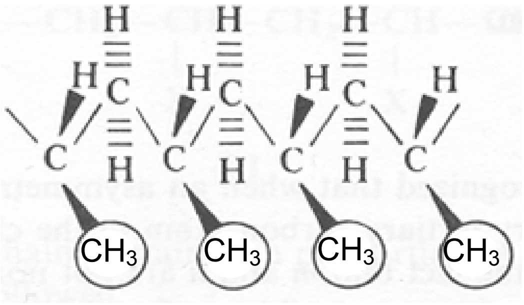
etc

termination: decomposition- and exchange reactions

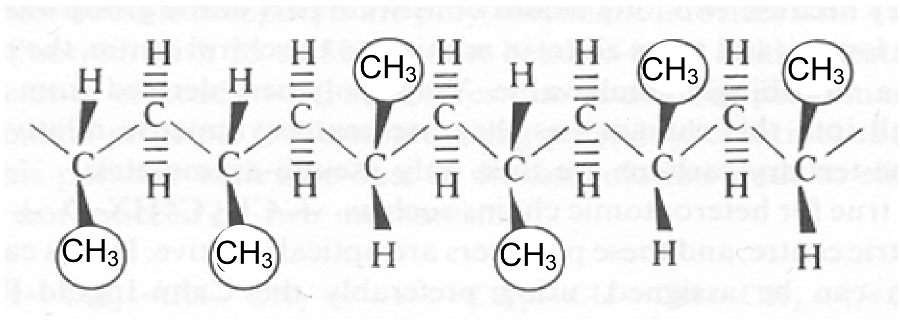
complexation only possible in certain sterical configurations, thus, opening a route for targeted synthesis of stereo-specific polymers.



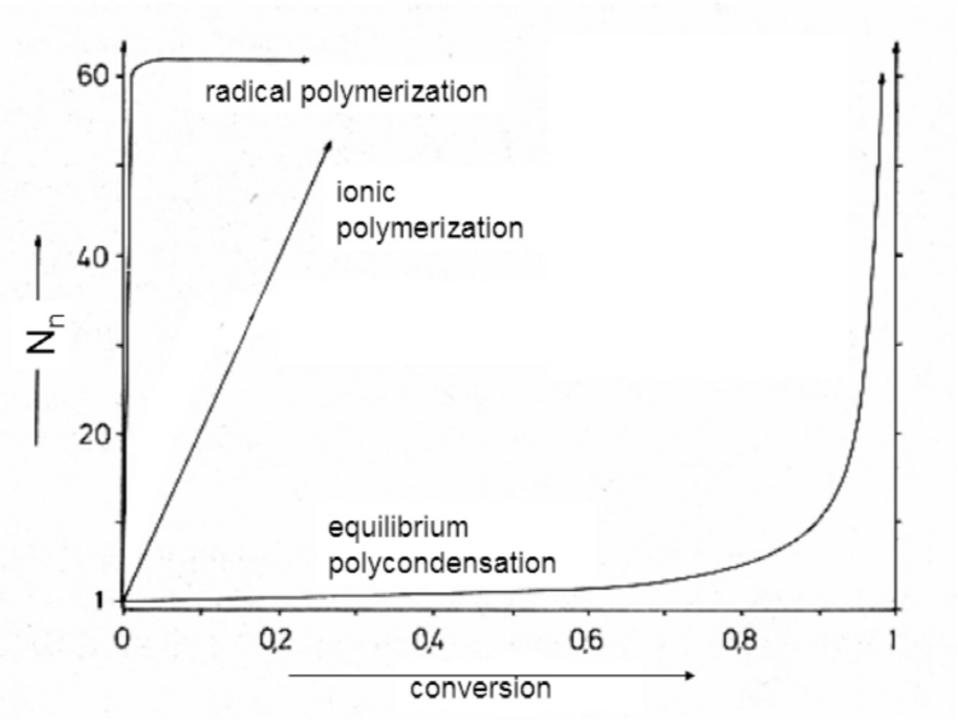
here: isotactic polypropylene



for comparison: atactic polypropylene



Number average as a function of conversion for different synthesis methods



Classification of polymerization methods

	step-growth (R-Reaction)	chain-growth (M-Reaction)
with (L-Reaction)	$P_i + P_j \rightarrow P_{i+j} + L$ Polycondensation	$P_i + M \rightarrow P_{i+1} + L$ Polymerization
without (O-Reaction)	$P_i + P_j \rightarrow P_{i+j}$ Polyaddition	$P_i + M \rightarrow P_{i+1}$ Polyelimination

production of reaction products L

Choice of synthesis method and varying control of termination reactions has significant impact on the distributions of the resulting molecular weights!

2.4 Determination of Molecular Weight Distributions

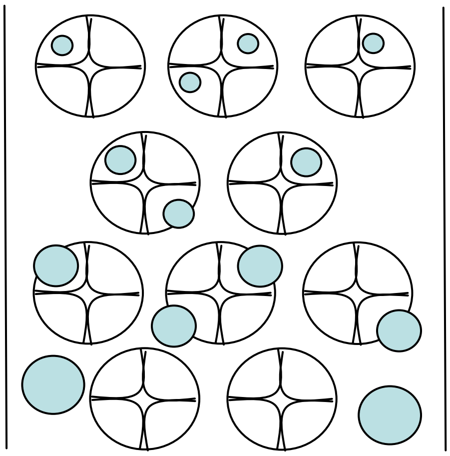
1.	Gel permeation chromatography (GPC)	distribution; M_w & M_n
2.	Ultracentrifugation	M_z & M_w
3.	Matrix assisted Laser Desorption/Ionisation- Time-of-Flight (MALDI - TOF)	distribution; M_w & M_n
4.	Scattering methods (see Chap. 5)	M_w
5.	Membrane osmometry (see Chap. 4)	M_n
6.	Viscosimetry	between M_w & M_n

2.4.1 Gel Permeation Chromatography (GPC)

also: SEC (Size or Steric Exclusion Chromatography)

Separation principle

$$V_e = V_0 + K_{SEC} V_i$$
$$0 \le K_{SEC} \le 1$$



with
V_e = elution volume
V_i = total pore volume
V_0 = volume outside pores

$K_{SEC} = 0$ for molecules bigger than largest pore size
$K_{SEC} = 1$ for small molecules for which the total pore volume V_i is accessbile.

GPC measures the hydrodynamic volume of a polymer $V_E \propto R_H$

Separation is due to changes in the Gibb's free enthalpy when crossing over from the mobile to the stationary phase:

$$\Delta G = \Delta H - T\Delta S = -k_B N_A T \ln K_{SEC}$$

with ΔH= enthalpy change and ΔS= entropy change

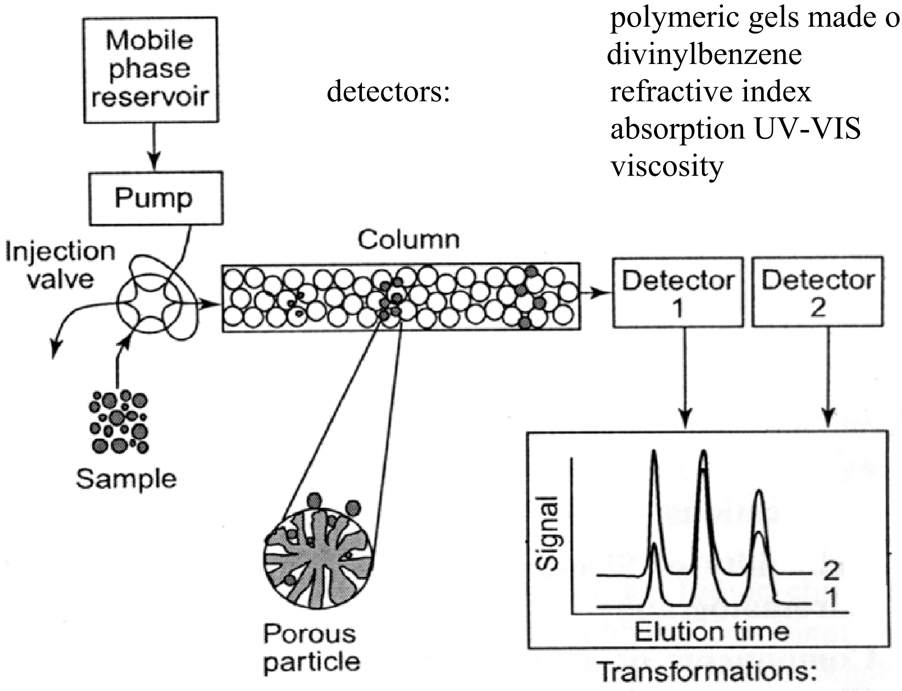
Ideally, separation is not due to interactions between polymer and column material, but is due to molecular weight dependent changes in entropy when crossing over from the mobile to the stationary phase.

Ideal separation results from changes in entropy only $\Delta H = 0$

$$K_{SEC} = \exp\left(-\frac{\Delta S}{k_B N_A}\right)$$

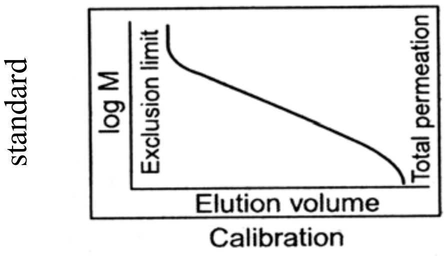
Experimental setup

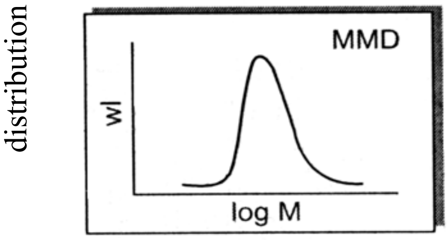
mobile phase:	good solvent for polymers
column:	porous material, such silica or swollen polymeric gels made of styrene & divinylbenzene
detectors:	refractive index absorption UV-VIS viscosity



transformations:

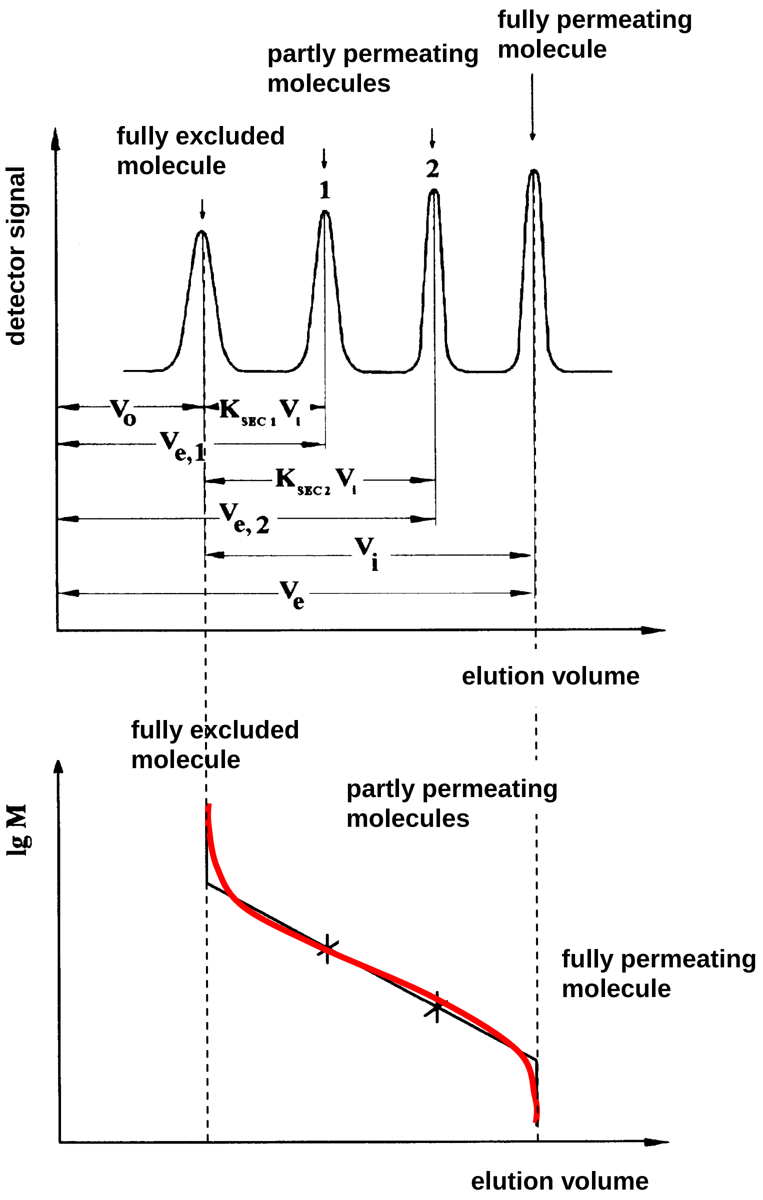
1. signal to concentration
2. time to elution volume
3. elution volume to molar mass





Calibration with defined standards

In a limited region there is a linear relation between log(M) and V_e $\quad \log M = A + BV_e$



Universal calibration

Elution volume V_E is proportional to the hydrodynamic radius R_H
R_H is proportional to the product of molecular weight M and intrinsic viscosity η

$$V_E \propto R_H \propto \eta M$$

Diagram, where the product M η is plotted versus V_e should lead to master curve for different polymers

$$(M_1\eta_1)_{V_e} = (M_2\eta_2)_{V_e}$$

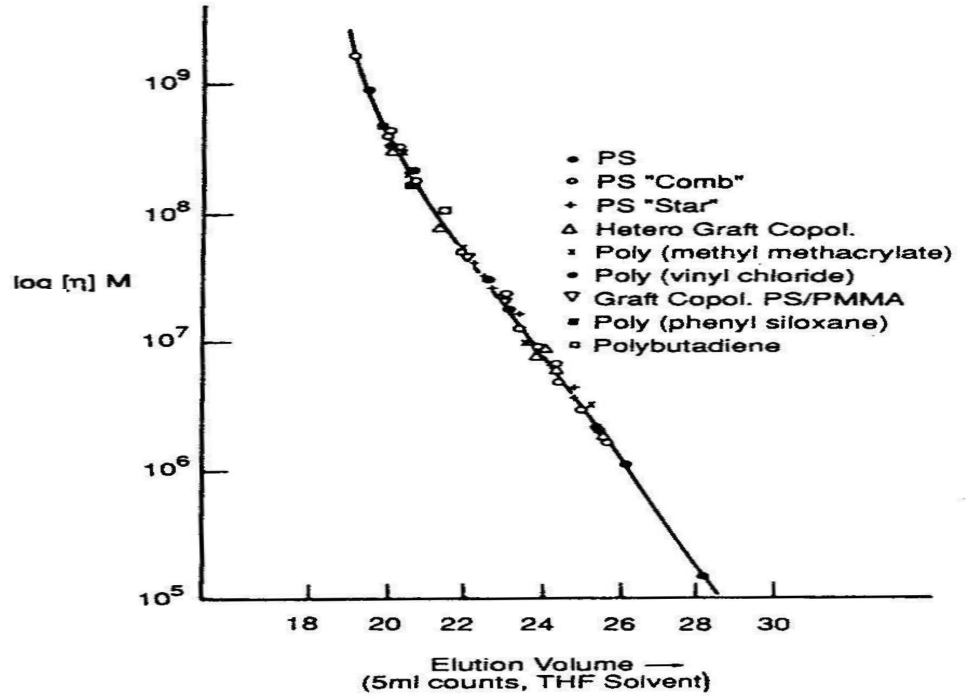
η is a function of molecular weight (Mark-Houwink relation): $\eta = cM^{\alpha}$

$$\Rightarrow \qquad (c_1 M_1^{\alpha_1+1})_{V_e} = (c_2 M_2^{\alpha_2+1})_{V_e}$$

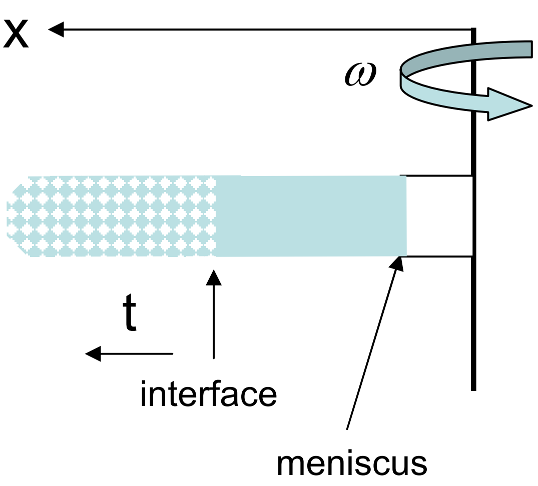
Calibration of the column with polymer 1 ⇒ molecular weight of second polymer if c_i and α_i are known (Literature: "Polymerhandbook")

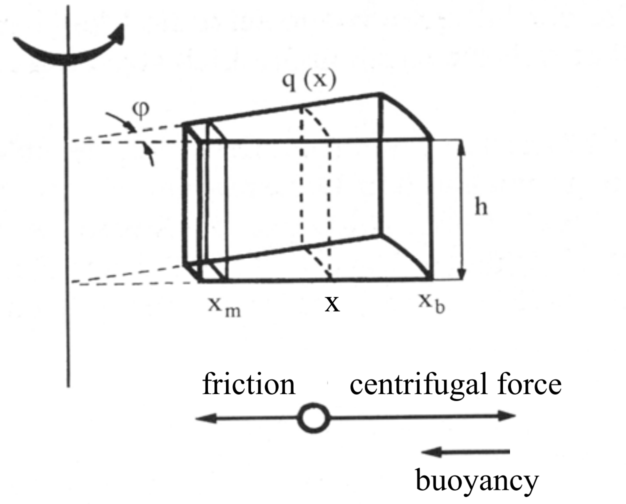
$$\ln M_2 = \frac{1}{1+\alpha_2}\ln\frac{c_1}{c_2} + \frac{1+\alpha_1}{1+\alpha_2}\ln M_1$$

universal calibration $M_2 = M_1 \dfrac{\eta_1}{\eta_2}$



2.5.2 Ultracentrifugation





f = friction coefficient
ω = angular velocity
D = diffusion coefficient
ρ_s = solvent density
υ_P = partial specific volume polymer

friction	$f\frac{dx}{dt}$
centrifugal force	$m_{eff}\,\omega^2 x$
buoyancy	$\frac{M}{N_A}\rho_S \upsilon_P \omega^2 x$

Measuring principle

Superposition of sedimentation and diffusion

1. Sedimentation velocity method

- fast rotation ≈ 60000rpm
- centrifugal acceleration stronger than diffusion
- temporal development of concentration profile is detected.
- "fast" (2h); diffusion coefficient needs to be known; complicated averages.

$\rho_{solvent} > \rho_{polymer}$ ⇒ flotation

$\rho_{solvent} < \rho_{polymer}$ ⇒ sedimentation

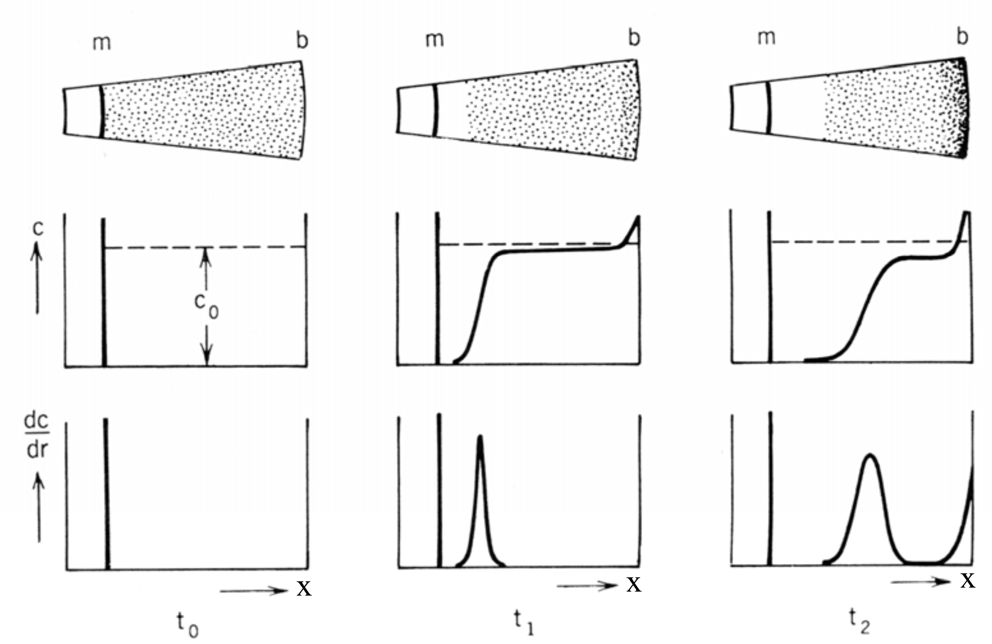
Ansatz balance of forces: centrifugal force = frictional force $m_{eff}\omega^2 x = f\,\frac{dx}{dt}$

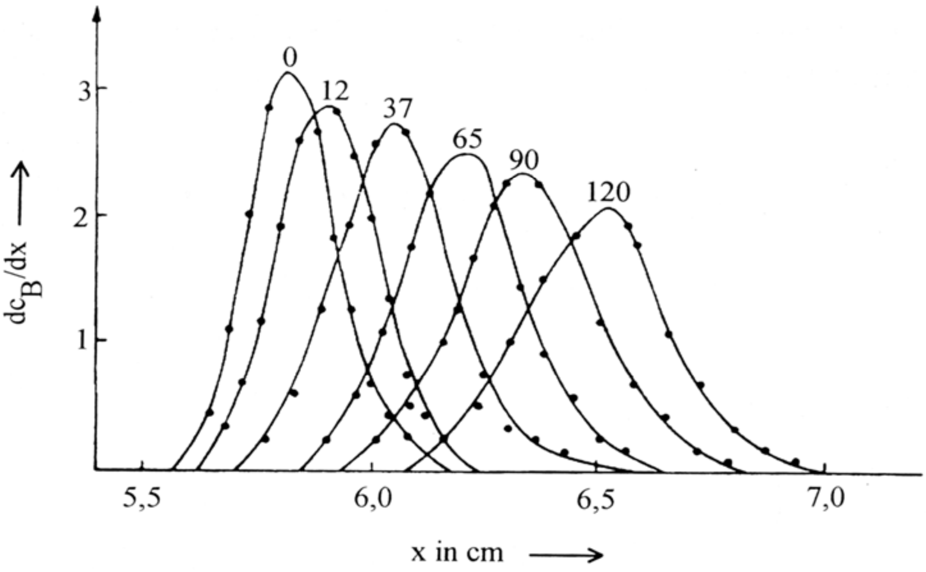
effective mass due to buoyant force $m_{eff} = \frac{M}{N_A}\left(1-\rho_S\upsilon_P\right)$

with $f = \frac{k_B T}{D}$, D determined by independent experiment dynamic light scattering

$$\boxed{M = \frac{{}^{dx}\!/_{dt}}{x}\,\frac{N_A\,k_B T}{\omega^2 D}\left(1-\rho_s\upsilon_P\right)^{-1}}$$

detection of profile with time





2. Sedimentation equilibrium method

- slower rotation < 20000rpm
- equilibrium between sedimentation and diffusion; radial concentration profile is detected.
- "time consuming" (24h); all averages can be determined.

in addition: diffusion mass current = sedimentation mass current

1. Fick`s law $\frac{dm_D}{dt} = -Dq\frac{\partial c}{\partial x} \quad = \quad \frac{dm_S}{dt} = cq\frac{\partial x}{\partial t} \quad \Rightarrow \quad c\frac{\partial x}{\partial t} = -D\frac{\partial c}{\partial x}$

with $M = \frac{dx/dt}{x}\frac{k_B N_A T}{\omega^2 D}\left(1-\rho_s \upsilon_P\right)^{-1}$

$$\frac{1}{c}\frac{\partial c}{\partial x} = \frac{\partial \ln c}{\partial x} = \frac{M\omega^2 x(1-\rho_s\upsilon_P)}{k_B N_A T}$$

$\Rightarrow \quad c = c(x_b)\exp\left[\frac{M}{2k_B N_A T}\left(1-\rho_s\upsilon_P\right)\omega^2(x^2-x_b^2)\right]$ monodisperse sample

for a polydisperse sample: $\frac{\partial c}{\partial x} = \frac{\omega^2 x(1-\rho_s\upsilon_P)}{k_B N_A T}\sum_i c_i M_i$

take average at each sample position x

$$M_w(x) = \frac{\sum_i c_i(x) M_i}{\sum_i c_i(x)} = \frac{\partial c}{\partial x}\frac{1}{c(x)}\frac{k_B N_A T}{\omega^2 x\left(1-\rho_s\upsilon_P\right)}$$

then integrate over whole sample

$$M_w = \frac{\int_{x_m}^{x_b} M_w(x) x c_i(x) dx}{\int_{x_m}^{x_b} x c_i(x) dx} = \frac{k_B N_A T\left[c(x_b)-c(x_m)\right]}{\omega^2\left(1-\rho_s\upsilon_P\right)\int_{x_m}^{x_b} x c_i(x) dx}$$

M_n and M_z analogous (see Arndt/Müller)

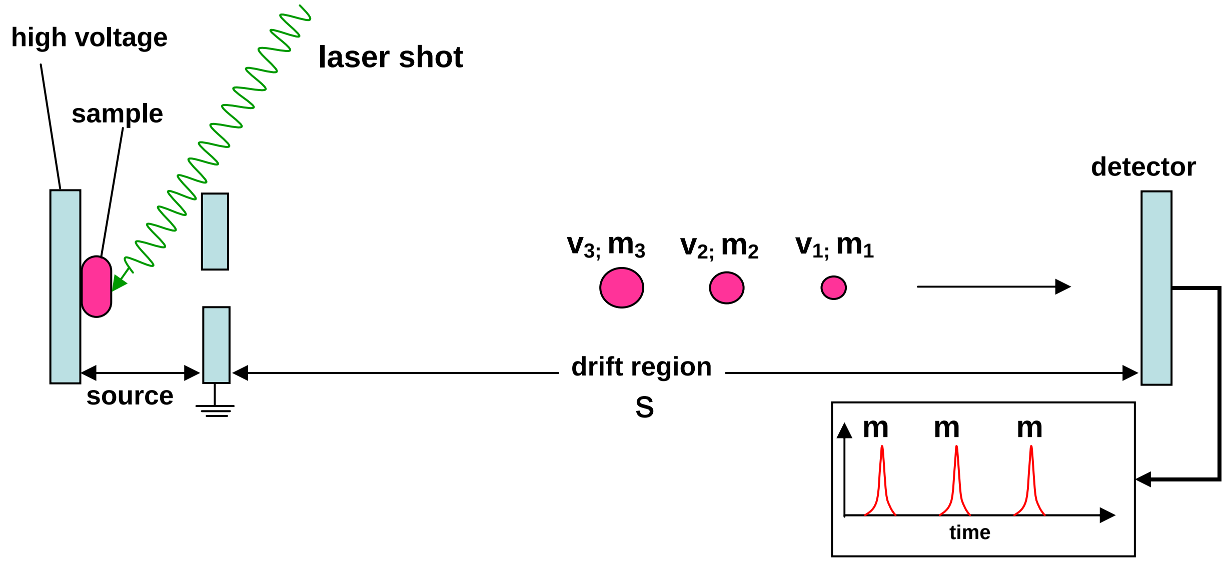
Ultracentrifugation is time-consuming (data collection & evaluation) and involves substantial experimental efforts.

When useful?

1. very large molecular masses; broad working range from 10^3 to10^7 g/mole.
2. polymers interacting with column material.
3. distinction between polymer mixtures and diblock-copolymers determination of chemical heterogeneity of block-copolymers density gradient.
4. size determination of polymeremulsions in water or organic solvents.

2.5.3 MALDI-TOF
Matrix Assisted Laser Desorption Ionization-Time-of-Flight Mass Spectrometry

Measuring principle



$$zV_0 = \frac{M}{2}v^2 = \frac{M}{2}\left(\frac{s}{t}\right)^2 \quad \Rightarrow \quad M = 2zV_0\left(\frac{t}{s}\right)^2$$

t = flight time;
s = flight path length (typically 1m)
z = charge
V_0= potential difference (typically 20 kV)
M = mass
v = velocity

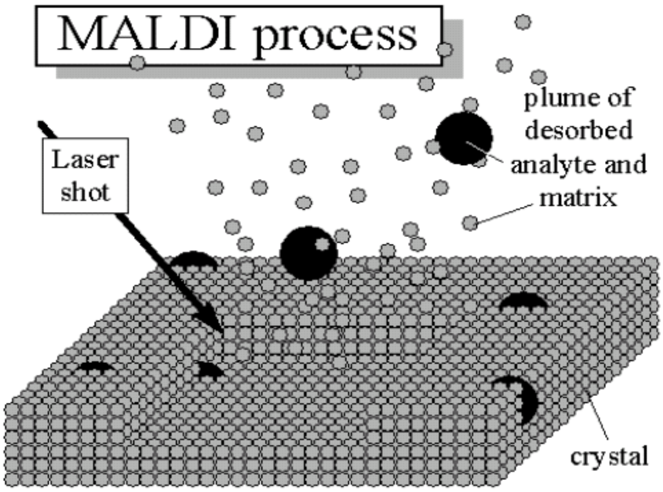
a mass difference of 1 amu correspond to a flight time of about 10 ns

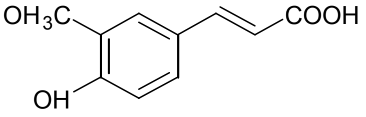
1 amu = $1.66053886 \cdot 10^{-27}$ kg ⇔ 1 g/mole

one monomer unit with a mass of approximately 100 g/mole has a flight time of 1μs.

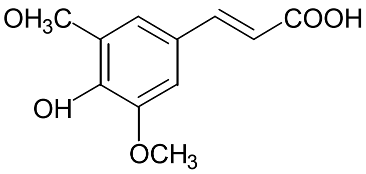
Matrix

1. must be activateable at laser wave length (about 330nm).
2. must transfer a proton to the polymer (proton donator).
3. must solve the polymer.
4. must not react with polymer.
5. is typically a crystalline solid material.





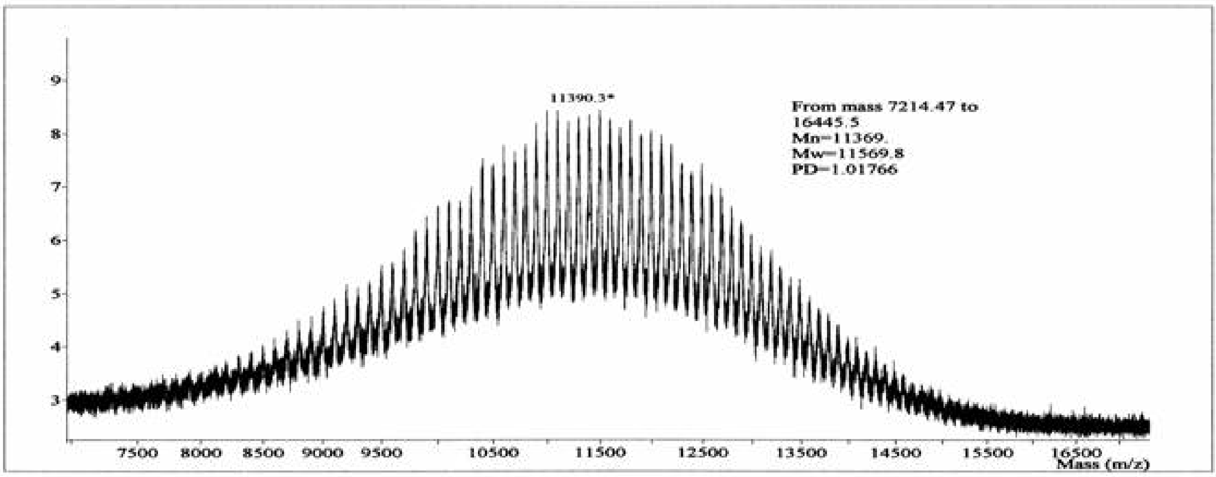
Ferulic acid



Sinapinic acid

Spectrum

e.g.: Poly(methylmethacrylate)



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for polymer analysis see also

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