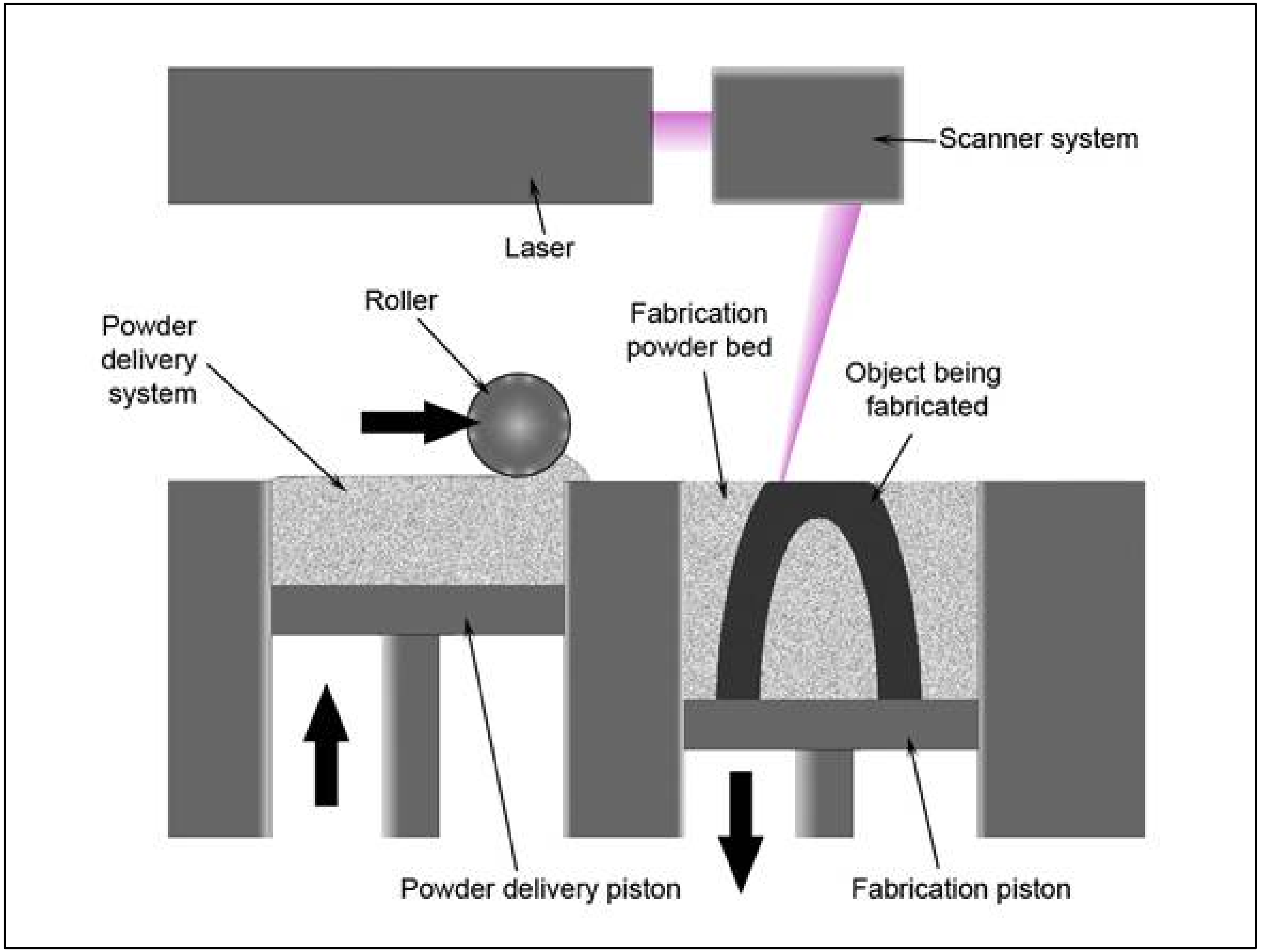
How Molecular Weight and Branching of Polymers Influences Laser Sintering Techniques

Dr. Bernd Tartsch

Malvern Instruments GmbH
Rigipsstr. 19, D-71083 Herrenberg
Tel: +49-7032-97 770, Fax: +49-7032-97 854
E-Mail: bernd.tartsch@malvern.com, www.malvern.de

Selective Laser sintering process

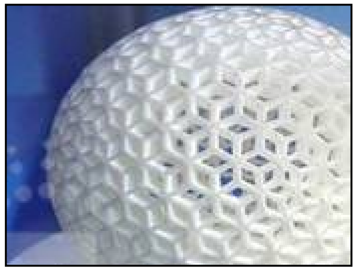


Quelle: Wikipedia, Materialgeeza

Laser sintering applications

- Prototyping
- Functional tests/build in tests
- Small serial production
- Interpenetrating parts


Quelle: NW Rapid Manufacturing


Quelle: Ebyton Technology


Quelle: Rapid Pro

Materials for laser sintering

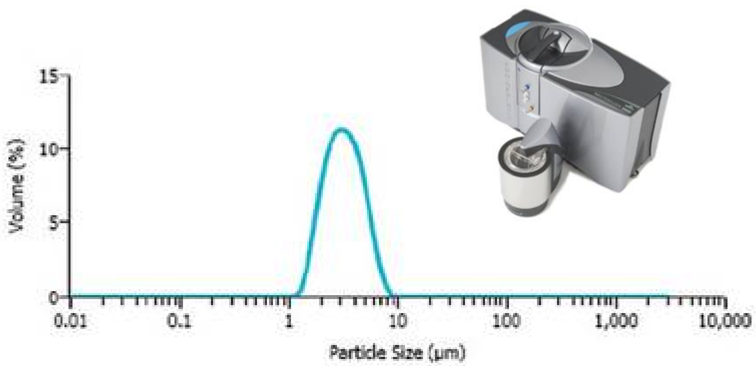
- Polyamide (modified)
  - high mechanical load capacity
  - temperature resistent (>150 °C)
  - resistent against bases, solvents, etc.
- filled with glass beads or mineral fibers
- Other thermoplastic elastomers

- Ceramics
- Metals

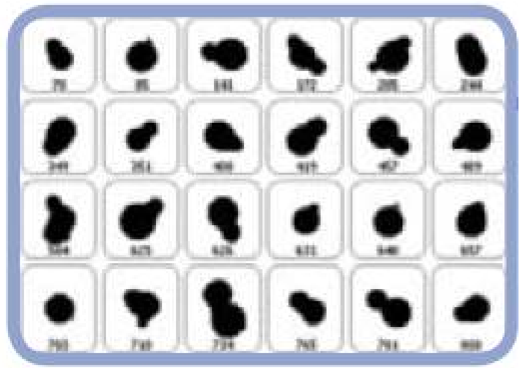
1. Challenge: Adding the next layer of material

- Particle size determines smallest structure size (0,1 mm)
- Particle size distribution and shape influences „flow“ of particles
- Best properties: regular, equi-axed, non-porous particles

Laser diffraction for particle size and size distribution



Automated optical particle size characterization system adds shape information



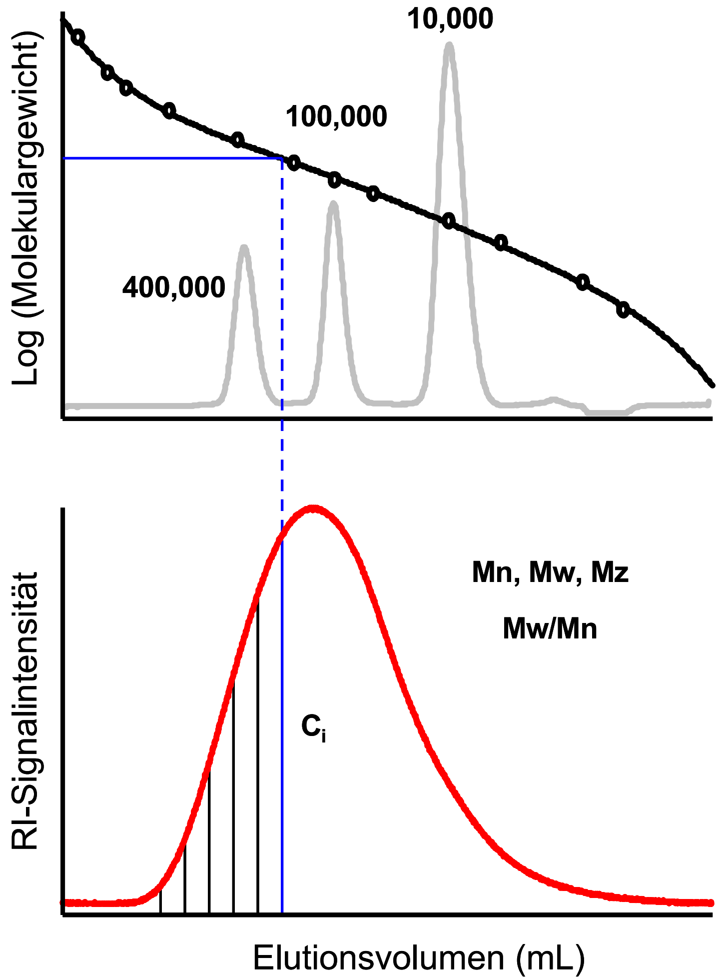
2. Challenge: Recycling of unused material

- Branching of polymer
- Degradation of polymer

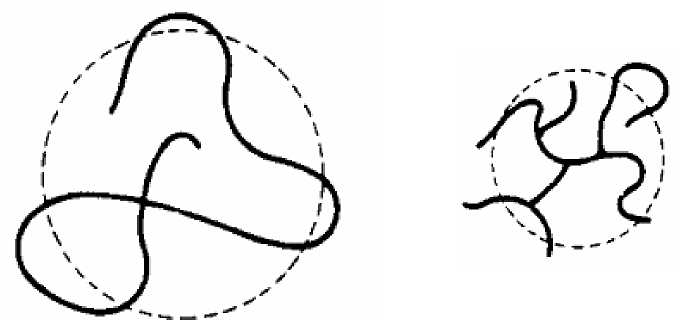
What do we need as an analytical tool?

⇒Triple detection size exclusion chromatography

Why can‘t we use conventional GPC with RI?



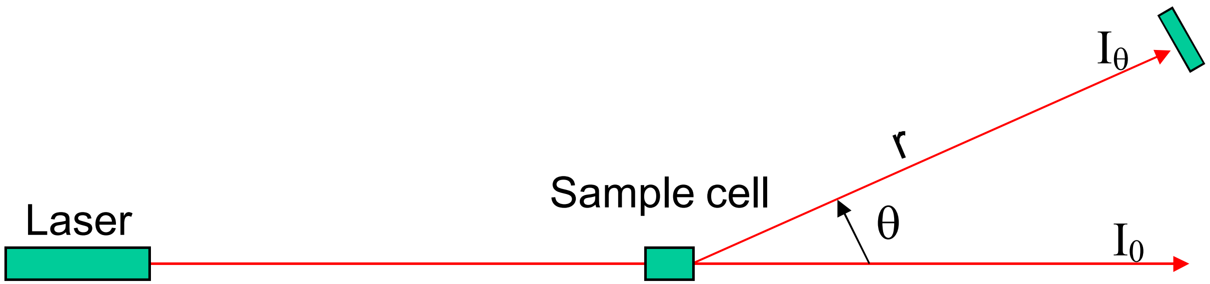
Potential branching destroys the relation between molecular weight and retention volume (hydrodynamic radius).



same Mw

different radius

Absolute Molecular Weight by Rayleigh Light Scattering

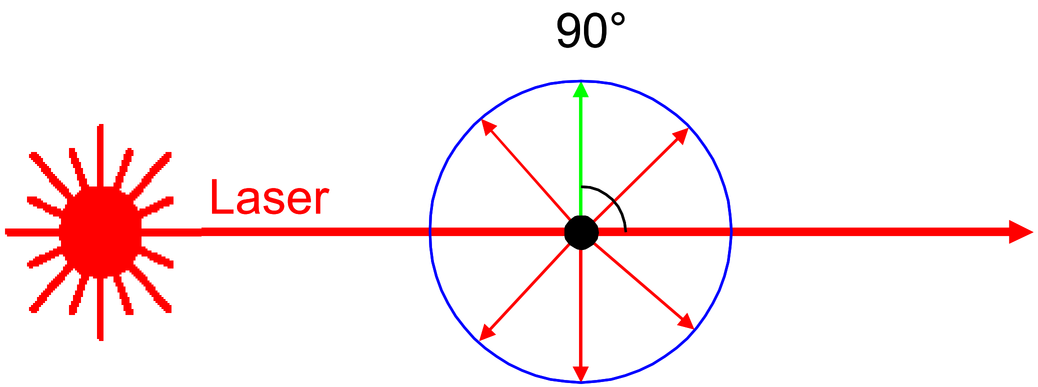


$$\frac{Kc}{R_\theta} = \frac{1}{M_w P_\theta} + 2A_2 c$$

$$K = \frac{2\pi^2 n_0^2}{N_A \lambda_0^4}\left(\frac{dn}{dc}\right)^2$$

R_θ	Rayleigh ratio I_θ/I_0 at angle θ
M_w	Weight average molecular weight
P_θ	Scattering function R_θ/R_0 (0...1)
c	Concentration
K	Optical constant
A_2	2. Virial coefficient
n_0	Refractive index of solvent
λ_0	Laser wavelength
N_A	Avogadro number
dn/dc	Refractive index increment

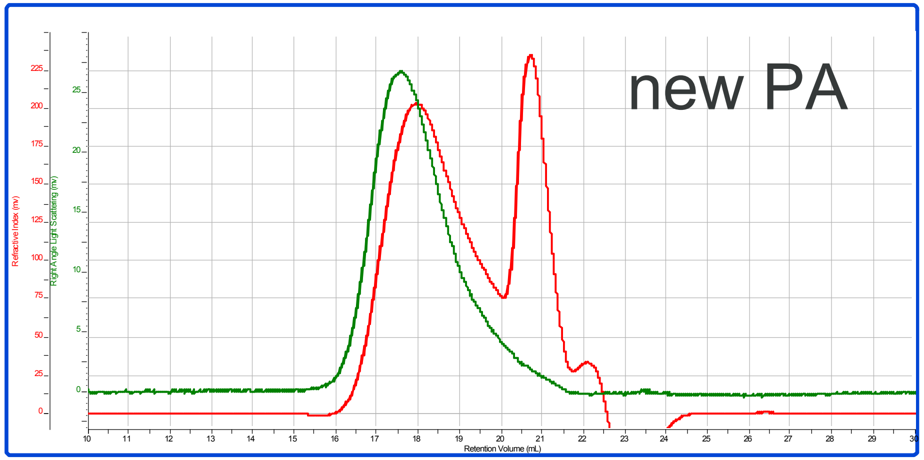
Angular Dependence



small molecules
radius < 15 nm
$P_\theta = 1$ for all θ

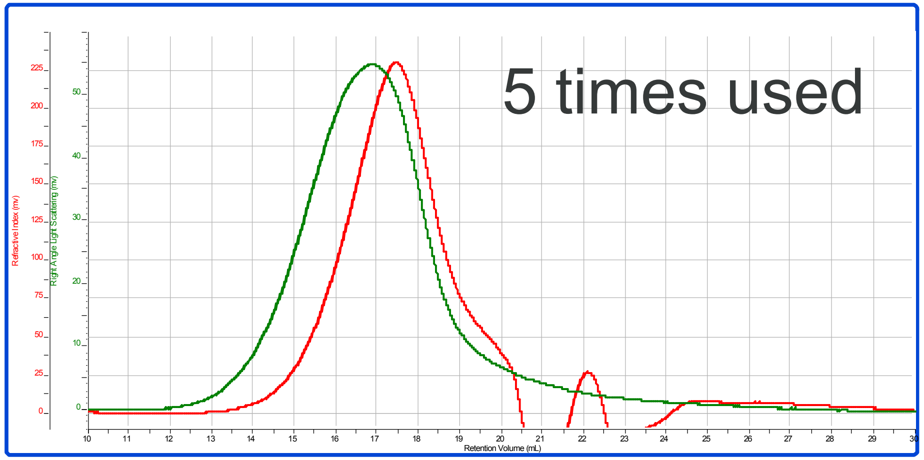
large molecules
radius > 15 nm
$P_\theta = 1$ for $\theta = 0°$

Molecular Weight Measurements



Mw = 36.200 g/mol

PDI = 1,23



Mw = 88.300 g/mol

PDI = 1,31

<u>Chromatographic conditions:</u>

Eluent: HFIP, 0.05 M K-acetate

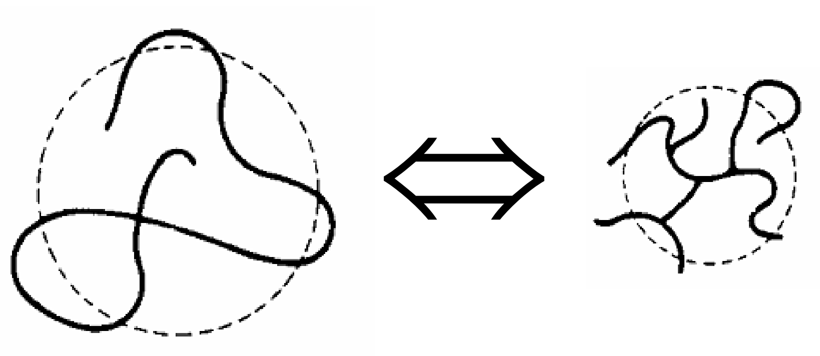
Columns: 2x I-MBHMW

Flow rate: 0,5 ml/min

Temperature: 45 °C

Malvern

What do we need for branching?
Zimm-Stockmayer-Theory



Light Scattering

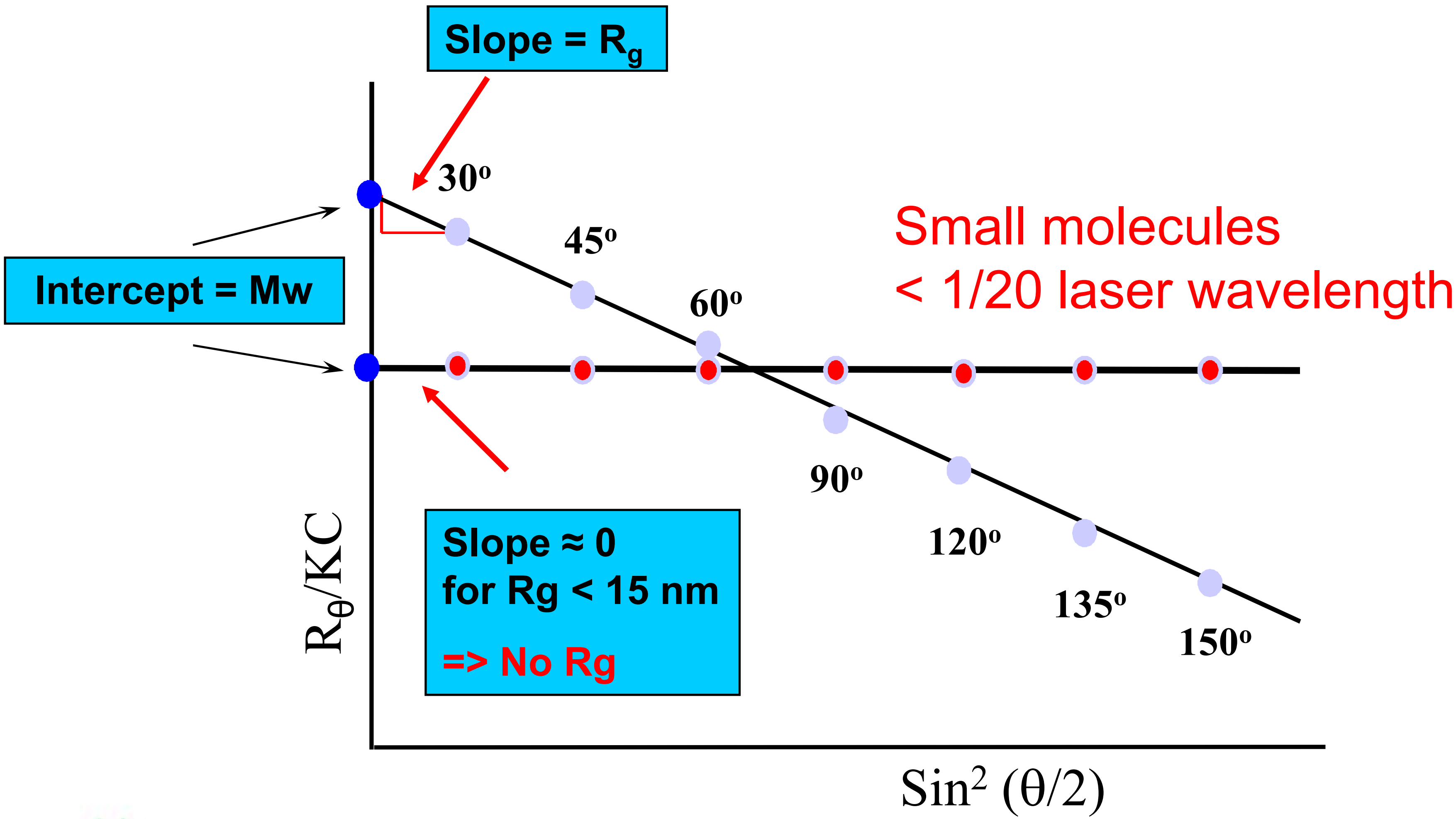
$$g = \left(\frac{R_G^2 \text{ (br)}}{R_G^2 \text{ (lin)}} \right)_M$$

Viscometer

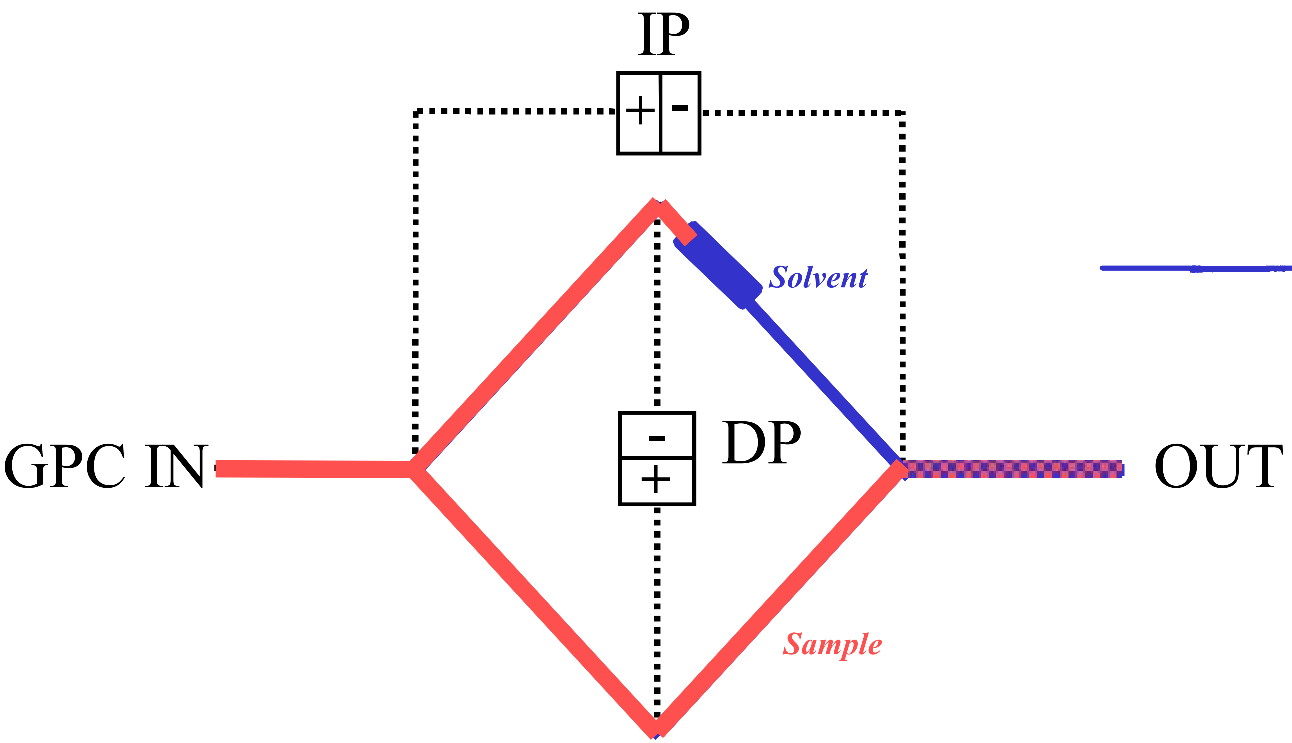
$$g = \left(\frac{[\eta](\text{br})}{[\eta](\text{lin})} \right)_M^{1/\varepsilon}$$

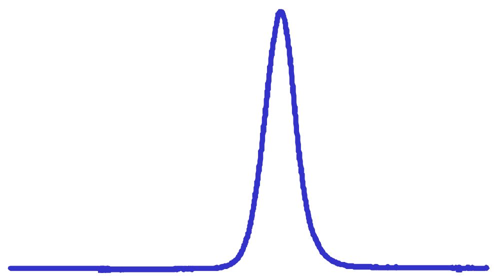
$$[\eta]M \propto R_h^3$$

Rg determination by Rayleigh Light Scattering



R_h or IV determination using the 4-Capillary Differential Viscometer





Wheatstone bridge concept
Max Haney, 1983

$$\eta_{sp} = \frac{4DP}{IP - 2DP} = C \times IV$$

Calculating the number of branches

B. H. Zimm, W. H. Stockmayer,, J. Chem. Phys 17, 1301 (1949).

1. star branching

$$g = \frac{3f - 2}{f^2}$$

f ... number of arms

2. trifunctional random – monodisperse in molecular weight

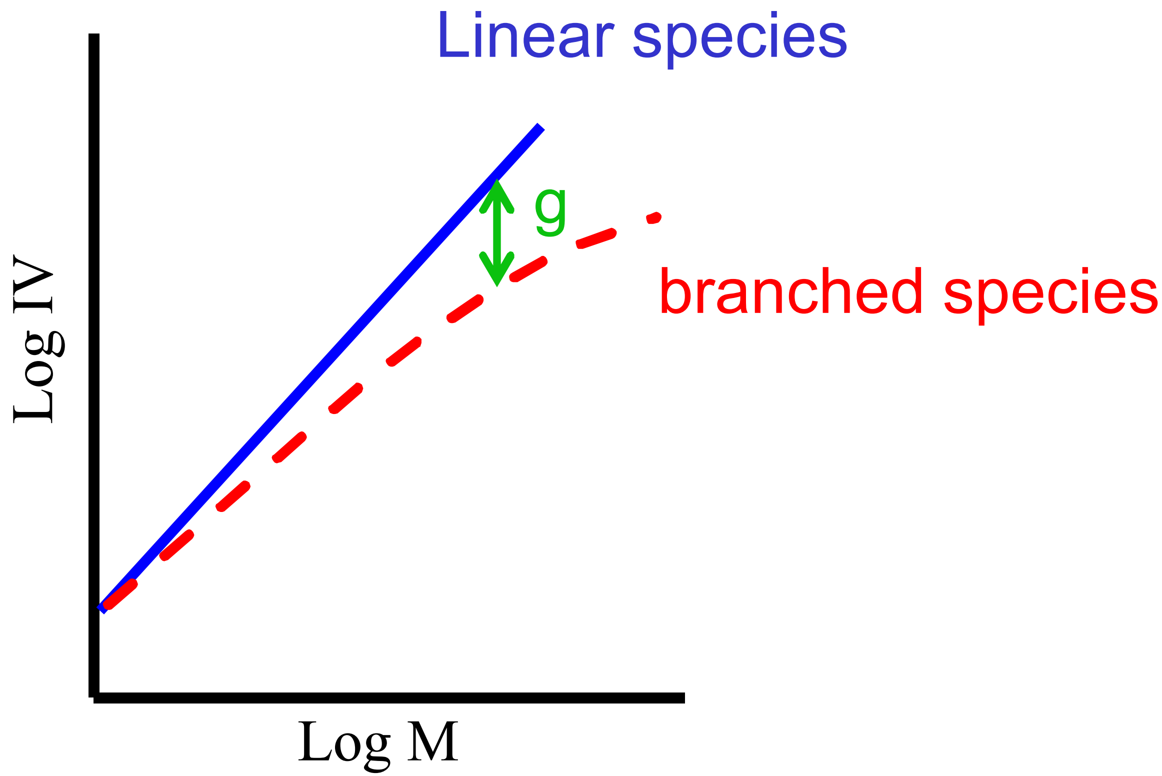
$$g = \left[\left(1 + \frac{B_n}{7} \right)^{1/2} + \frac{4B_n}{9} \right]^{-1/2}$$

B_n ... number of branches

3. trifunctional random – polydisperse in molecular weight

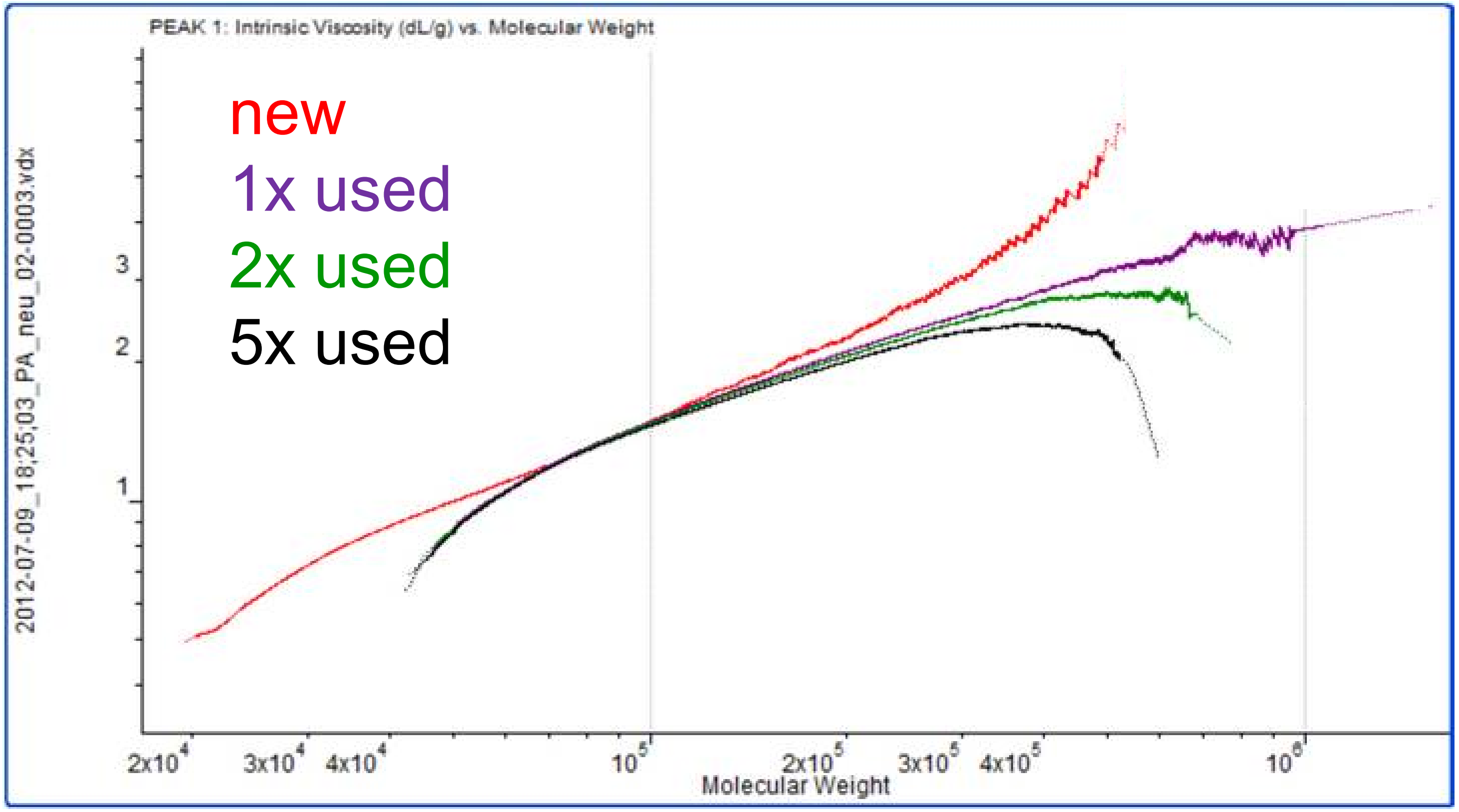
$$g = \frac{6}{B_n} \left[\frac{1}{2} \left(\frac{2 + B_n}{B_n} \right)^{1/2} \ln \left(\frac{(2 + B_n)^{1/2} + B_n^{1/2}}{(2 + B_n)^{1/2} - B_n^{1/2}} \right) - 1 \right]$$

Mark-Houwink-Plot or Branching View



Quelle: Wikipedia, Materialgeeza

Mark-Houiwnk-Plot of new and used PA



Numeric Results

Samples	Mw	PDI	Branches
new	36.200	1,23	Linear reference
1x used	52.400	1,28	1,18
2x used	65.700	1,27	1,43
5x used	88.300	1,31	1,89

⇒ Now the the data can be related with the behaviour in the laser sintering process and the amount of material that can be mixed with new material can be determined

Summary

- GPC with triple detection provides a tool to determine the amount of material that can be recycled in a laser sintering process
- Static Light Scattering is necessary in order to determine the absolute Mw of the branched polymers
- Viscosity detection is necessary in order to measure branching of the polymers
- In this case, the laser sintering process leads to a increase in molecular weight due to formation of branched structures.

Thank you

for your attention