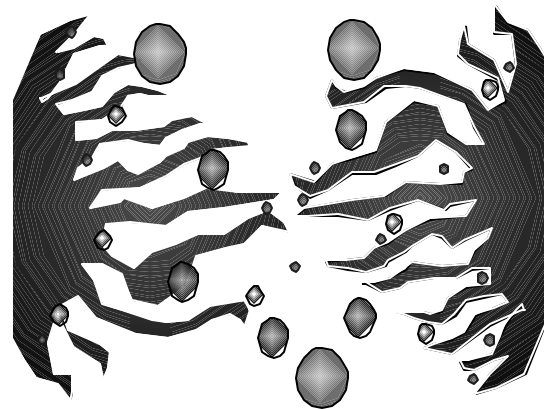


Tools For Polymer Characterization



Size Exclusion

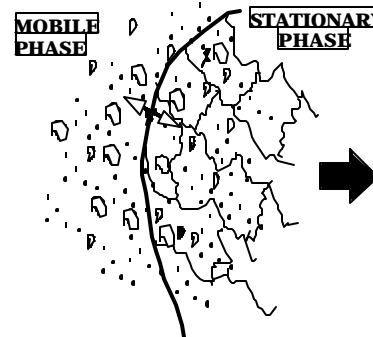


Gel Permeation / Size Exclusion / Gel Filtration - GPC / SEC / GFC

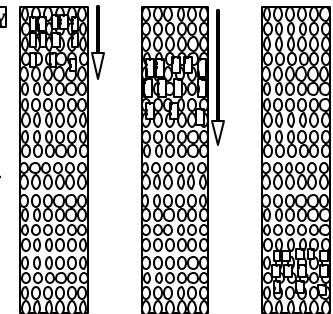
- GPC polymers
 - SEC polymers & proteins
 - GFC proteins
- Separation based on molecular size in solution
 - Order of elution - larger < small
 - Relatively low resolution method
 - Very predictable chromatography
 - If it can be dissolved, it can be analyzed

SIZE EXCLUSION CHROMATOGRAPHY

PRINCIPLE OF SEPARATION

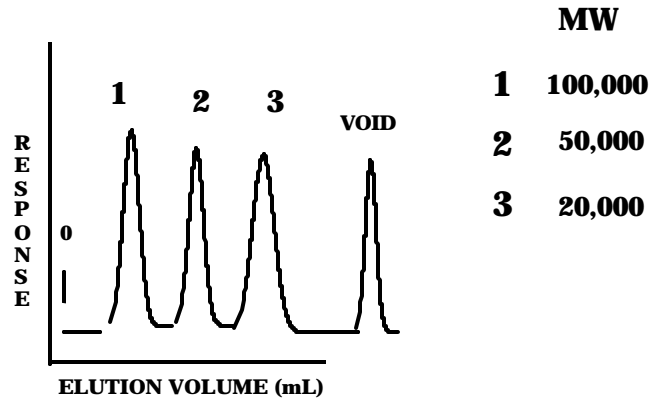


SEPARATION PROCESS

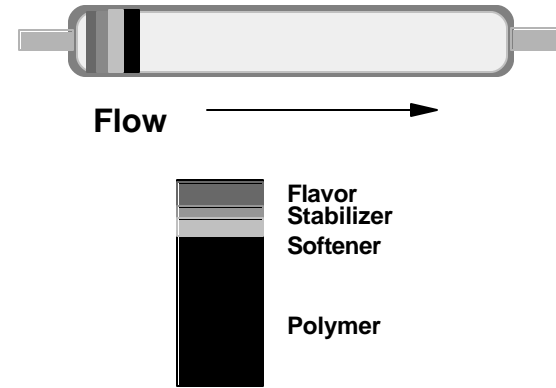


**ELUTION ORDER:
LARGER ELUTE FIRST**

ELUTION ORDER IN SIZE EXCLUSION (GPC)



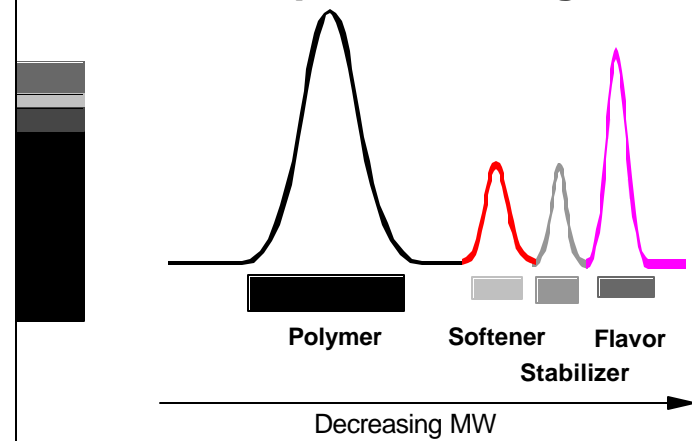
How GPC Works



How GPC Works



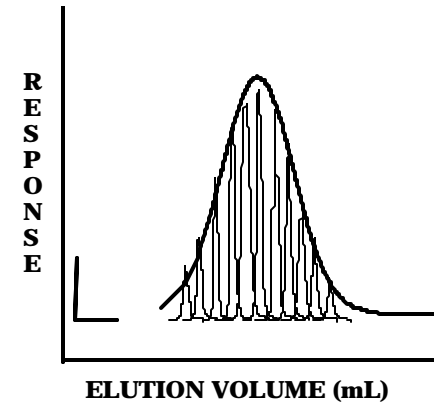
GPC Example - Chewing Gum



Molecular Weight Distribution

- ▶ Polymers have a distribution of various chain lengths, and, therefore, molecular weights.
- ▶ Monomers have a single molecular weight, and are monodisperse.
- ▶ This distribution of molecular weights results in an "Envelope" of elution from a column set.

MOLECULAR WEIGHT DISTRIBUTION



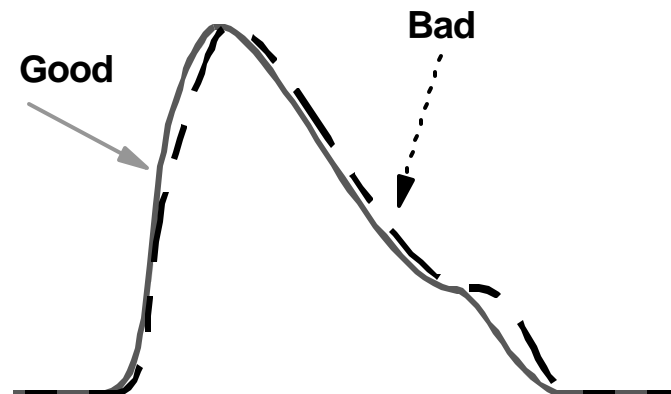
Why GPC?

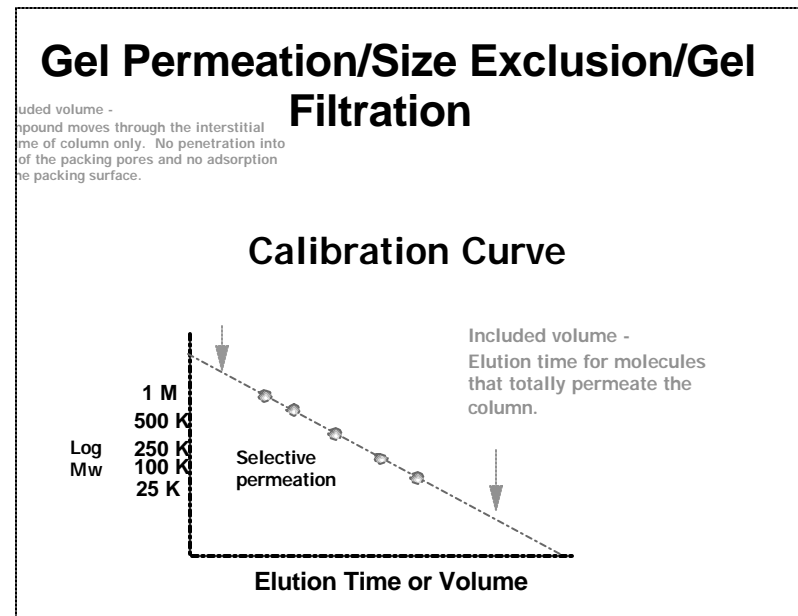
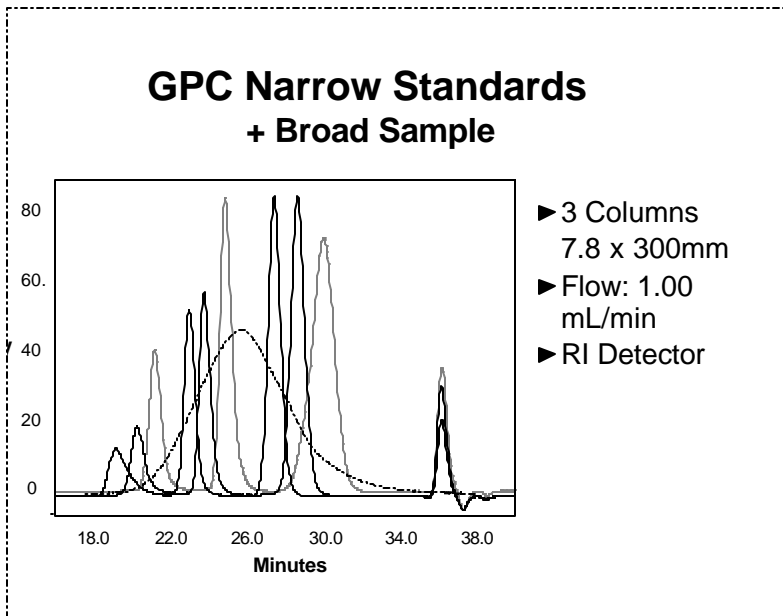
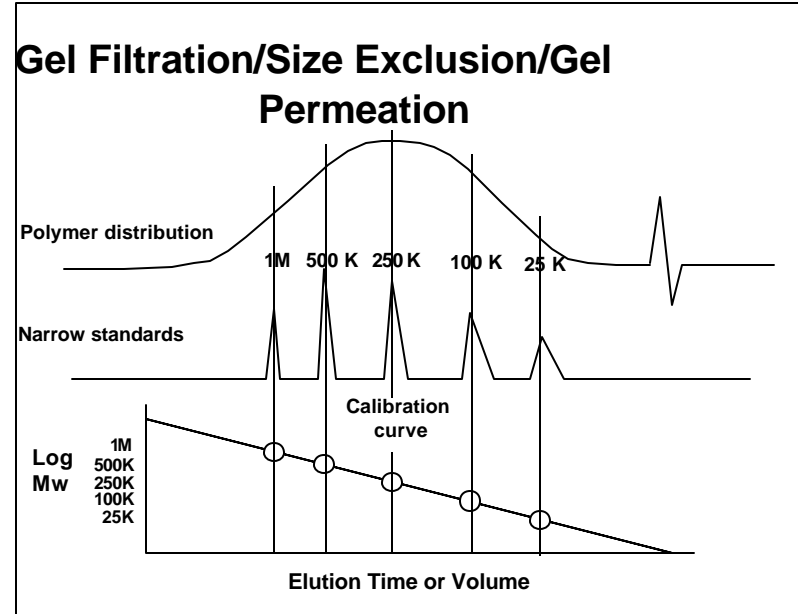
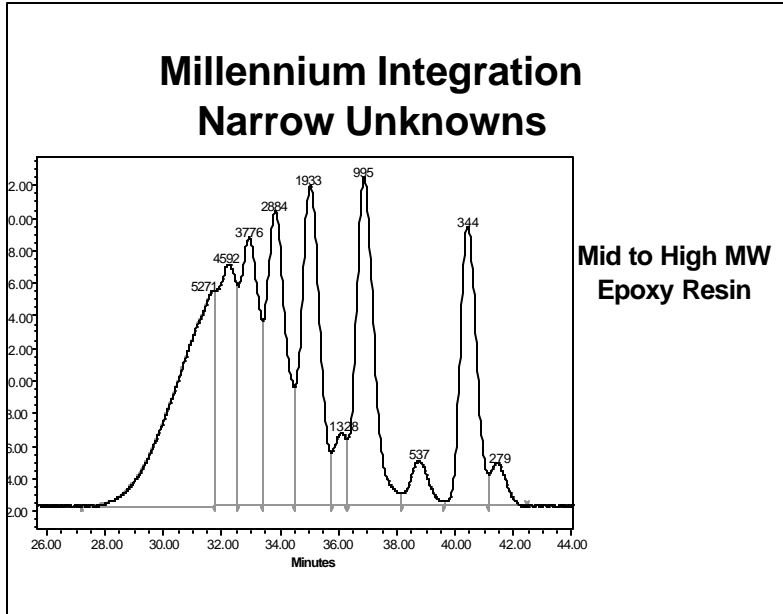
"Molecular Weight Distribution correlates with virtually all key processing characteristics and performance properties of a material."



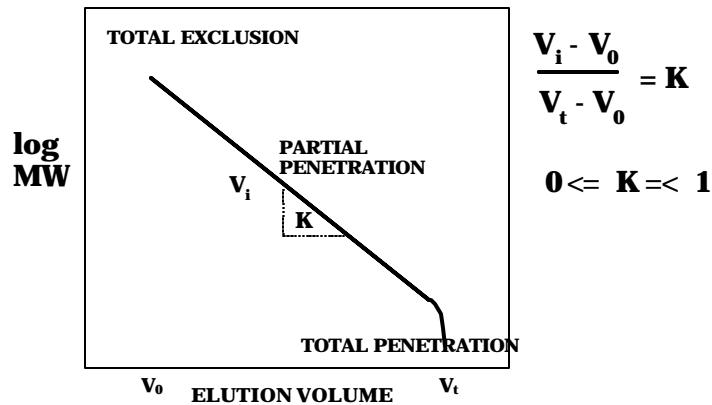
Plastics Technology, May 1986

Comparison of Results





THEORETICAL CURVE OF THE STERIC EXCLUSION



Gel Permeation / Size Exclusion / Gel Filtration - GPC / SEC / GFC

- There should be no interaction between the media surface and the sample.
- The same molecule can have different radii in different solvents.

GPC/SEC Separations

GPC is a SIZE separation technique.

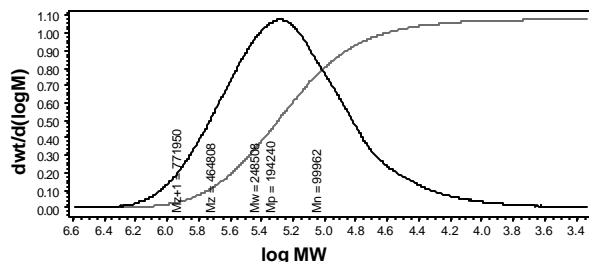
Separation is based on size in solution, not molecular weight.

Polymer size in solution is dependent on solvent and temperature.

Distribution Shapes

- ▶ Polymers may elute in many different shapes.
- ▶ Typical shapes are: Gaussian, Multi-Modal, Skewed-High, Skewed-Low.
- ▶ The various shapes may define important characteristics such as processing parameters and physical properties.

Molecular Weight Distribution



Slice Table - DOW 1683

#	Retention Time (min)	Adjusted RT (min)	Mol Wt (Daltons)	Log Mol Wt	Cumulative % (%)	Area	Outside Vo-Vt
1	19.550	19.550	1690819	6.228097	0.155	498	No
2	20.750	20.750	711461	5.852151	4.745	9695	No
3	21.950	21.950	294563	5.469178	28.585	29920	No
4	23.150	23.150	122389	5.087743	67.276	28261	No
5	24.350	24.350	52049	4.716409	89.878	10265	No

Calculation of MW Averages

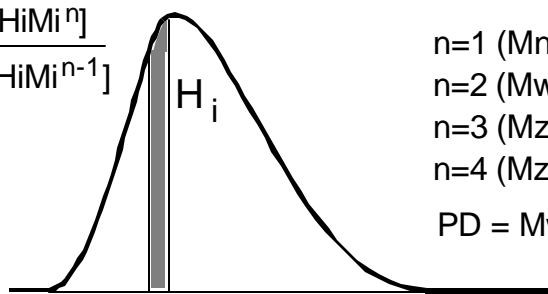
- ▶ Slices (heights, H_i) are drawn from the chromatogram baseline to the distribution curve, (usually >100).
- ▶ Slice heights are multiplied by the corresponding MW's, and summed, ($\sum [H_i M_i]$)
- ▶ Statistical averages are then calculated to obtain each MW moment:

$$\frac{\sum [H_i M_i^n]}{\sum [H_i M_i^{n-1}]};$$

Where $n=1$ is M_n , $n=2$ is M_w , $n=3$ is M_z .

Calculation of MW Averages

$$\bar{M}_x = \frac{\sum [H_i M_i^n]}{\sum [H_i M_i^{n-1}]}$$

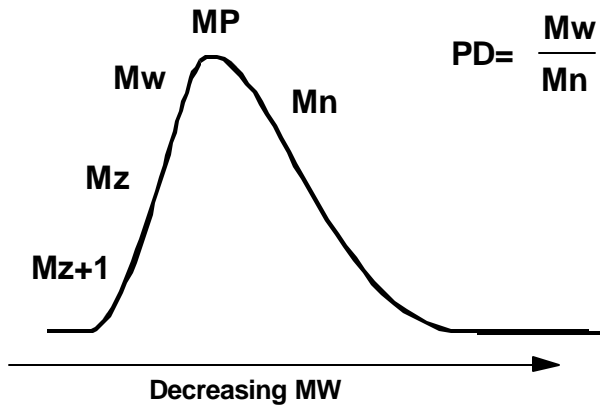


- $n=1$ (M_n)
- $n=2$ (M_w)
- $n=3$ (M_z)
- $n=4$ (M_{z+1})
- PD = M_w/M_n

Molecular Weight Moments

- ▶ 1st Moment = M_n (Number Average)
- ▶ 2nd Moment = M_w (Weight Average)
- ▶ 3rd Moment = M_z (Z Average)
- ▶ 4th Moment = M_{z+1} (Z+1 Average)
- ▶ M_w/M_n = Dispersity
- ▶ Moments are related to physical properties.

Molecular Weight Distribution



Physical Properties

- ▶ M_n is related to brittleness, flow properties, compression set.
- ▶ M_w is related to strength properties, (tensile, impact resistance).
- ▶ M_z is related to elongation and flexibility.
- ▶ M_{z+1} is related to die swell.

Importance of MWD

Property/Process Parameter	Effect of High MW	Effect of Low MW
<i>Impact Strength</i>	↑	↓
<i>Melt Viscosity</i>	↑	↓
<i>Processing Temp</i>	↑	↓
<i>Flex Life</i>	↓	↑
<i>Brittleness</i>	↑	↓
<i>Drawability</i>	↓	↑
<i>Softening Temp</i>	↑	↓
<i>Stress-crack Resistance</i>	↓	↑
<i>Melt Flow</i>	↓	↑

Polymer Concentrations for GPC

- ▶ $MW > 1,000,000$ _____ 0.007 - 0.02%
- ▶ 500K - 1,000,000 _____ 0.02 - 0.07%
- ▶ 100K - 500K _____ 0.07 - 0.10%
- ▶ 50K - 100K _____ 0.10 - 0.13%
- ▶ 10K - 50K _____ 0.13 - 0.16%
- ▶ < 10K _____ 0.16 - 0.20%

Sample Preparation

- ▶ Solvent must allow polymer chains to open up into the "most relaxed" conformation.
- ▶ Allow sufficient time for chains to unfold (>3 hours for some polymers).
- ▶ The greater the MW and crystallinity, the longer the time needed.
- ▶ High temperature, may be needed for highly crystalline polymers.

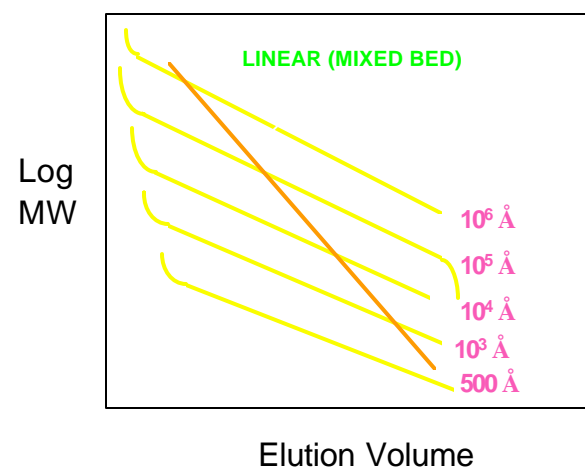
Sample Prep (cont'd)

- ▶ The polymer solution should be filtered unless there may be a chance of shear.
- ▶ To enhance dissolution, some light swirling (no vigorous shaking) may be done.
- ▶ Narrow standard solutions need not be filtered, and high molecular weight standards should not be shaken at all.
- ▶ An in-line filter may be used, but a pre-column is not recommended.

Column Selection

- | | | |
|------------------|-------|-------------------|
| ▶ MW 100 - 1,000 | _____ | 50A |
| ▶ MW 250 - 2,500 | _____ | 100A |
| ▶ MW 1,000 - 18K | _____ | 500A |
| ▶ MW 5,000 - 40K | _____ | 10 ³ A |
| ▶ MW 10K - 200K | _____ | 10 ⁴ A |
| ▶ MW 50K - 1M | _____ | 10 ⁵ A |
| ▶ MW 200K - >5M | _____ | 10 ⁶ A |
| ▶ 500K - ~20M | _____ | 10 ⁷ A |

ELUTION CURVES OF VARIOUS STATIONARY PHASES



Effective Molecular Weight Range: 10^1 10^2 10^3 10^4 10^5 10^6 10^7

Styragel HR 5E
Styragel HR 4E
Styragel HR 4
Styragel HR 3
Styragel HR 2
Styragel HR 1
Styragel HR 0.5

Styragel HR Series - 5 μ m

Effective Molecular Weight Range: 10^1 10^2 10^3 10^4 10^5 10^6 10^7

Low Molecular Weight Analysis
Molecular weight range: up to 4×10^6
Additives Epoxies Oligomers
Phenolics Urea/Formaldehyde
Melamine resins Ethanolamines
Unsaturated Polyesters

Press the Column Types to View Calibration Curve

PREVIOUS INFO MENU

Waters

