Topic 7. Molecular weight measurement

Expected learning outcomes:
By the end of this lesson, student should be able to…

- discuss and explain the experimental method to measure the molecular weight distribution of polymers
- discuss and explain basic principles of GPC operation
- understand and discuss the rationale for separation of polymer chains by size and the role of detectors in GPC
- apply methods of calibration to GPC, including the universal calibration curve

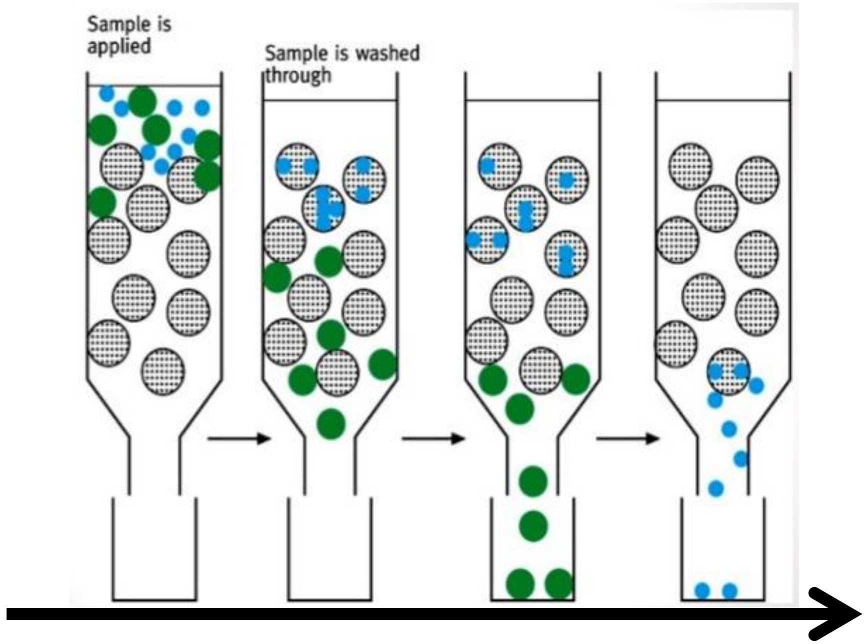
Topic 7. Molecular weight measurement

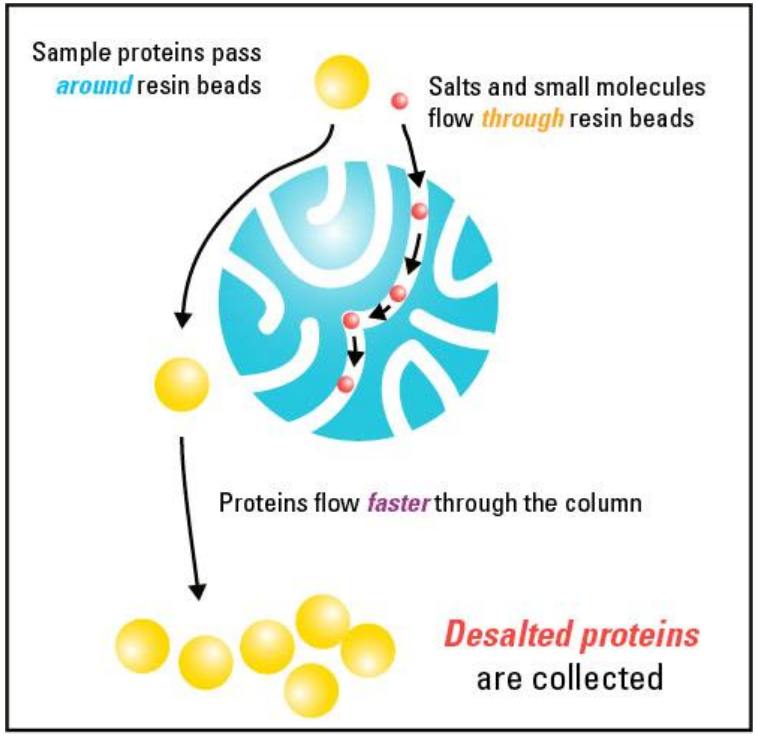
Sub-Topics:

7.1 Principles of gel permeation chromatography (GPC)
7.2 Parts of GPC and calibration
7.3 Universal calibration curve

- 7.3.1 Universal calibration curve – calibration with standards of same polymer
- 7.3.2 Universal calibration curve – calibration with standards of different polymer
- 7.3.3 Universal calibration curve – calibration with viscosity

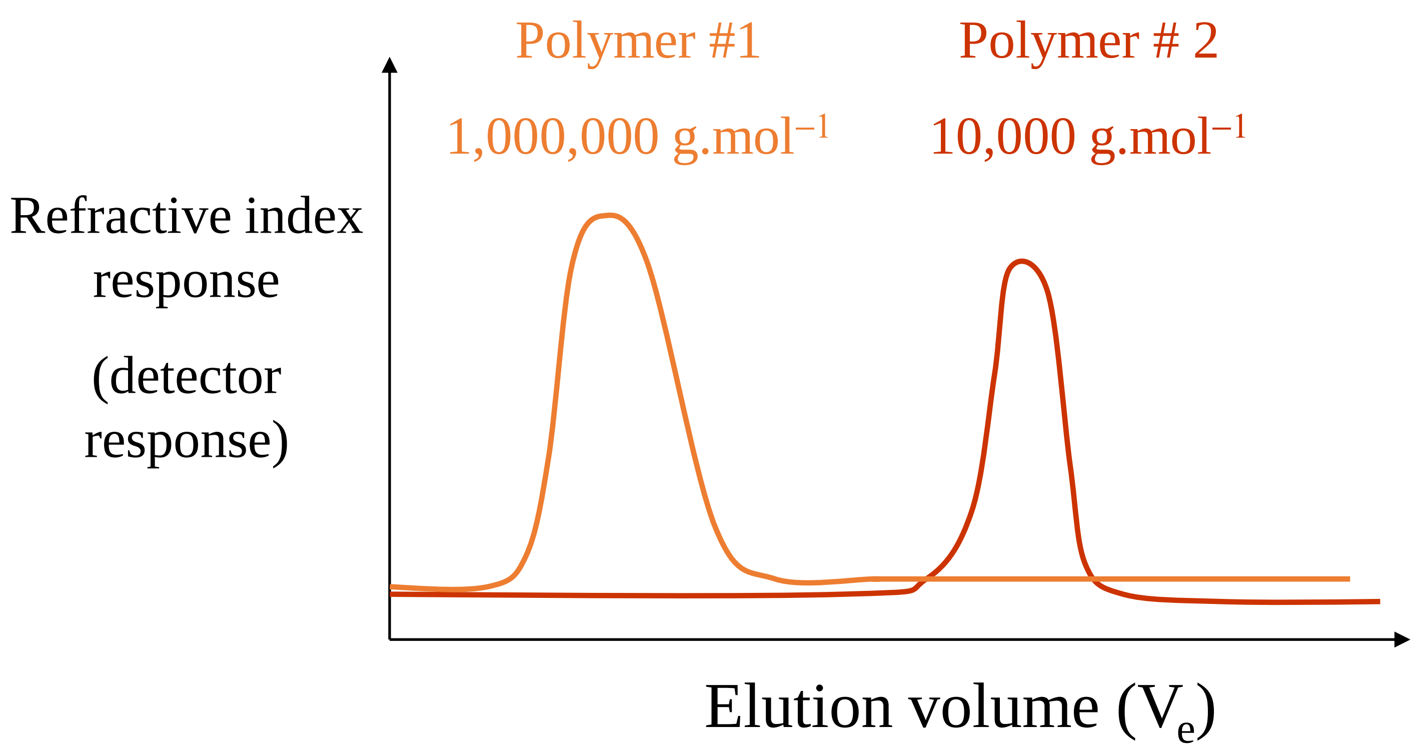
Separation based on molecular weight



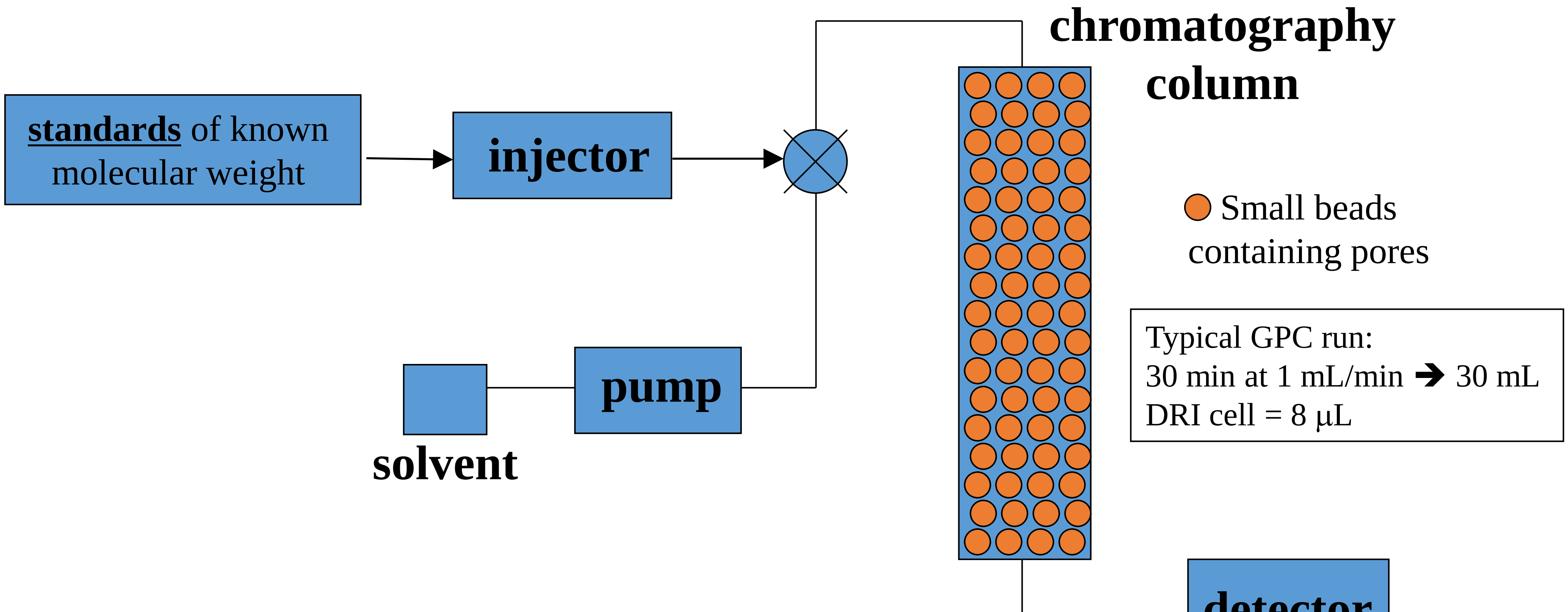


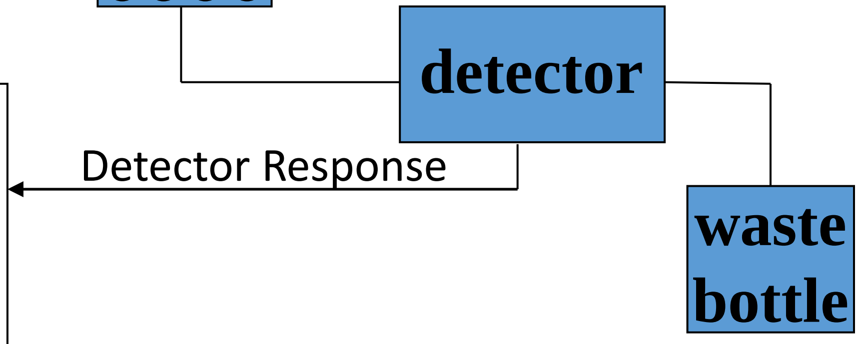
- The smaller polymer chains take longer time than the larger polymer chains to go through all the pores.
- The polymer chains with small size elute at longer times.

Gel Permeation Chromatography (GPC):

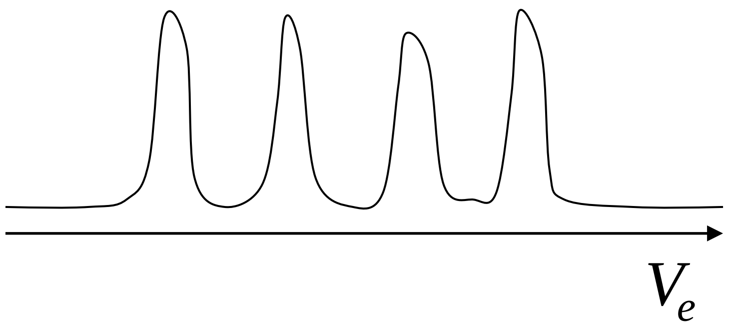


- The smaller polymer chains take longer time than the larger polymer chains to go through all the pores.
- The polymer chains with small size elute at longer times (or larger elution volumes).

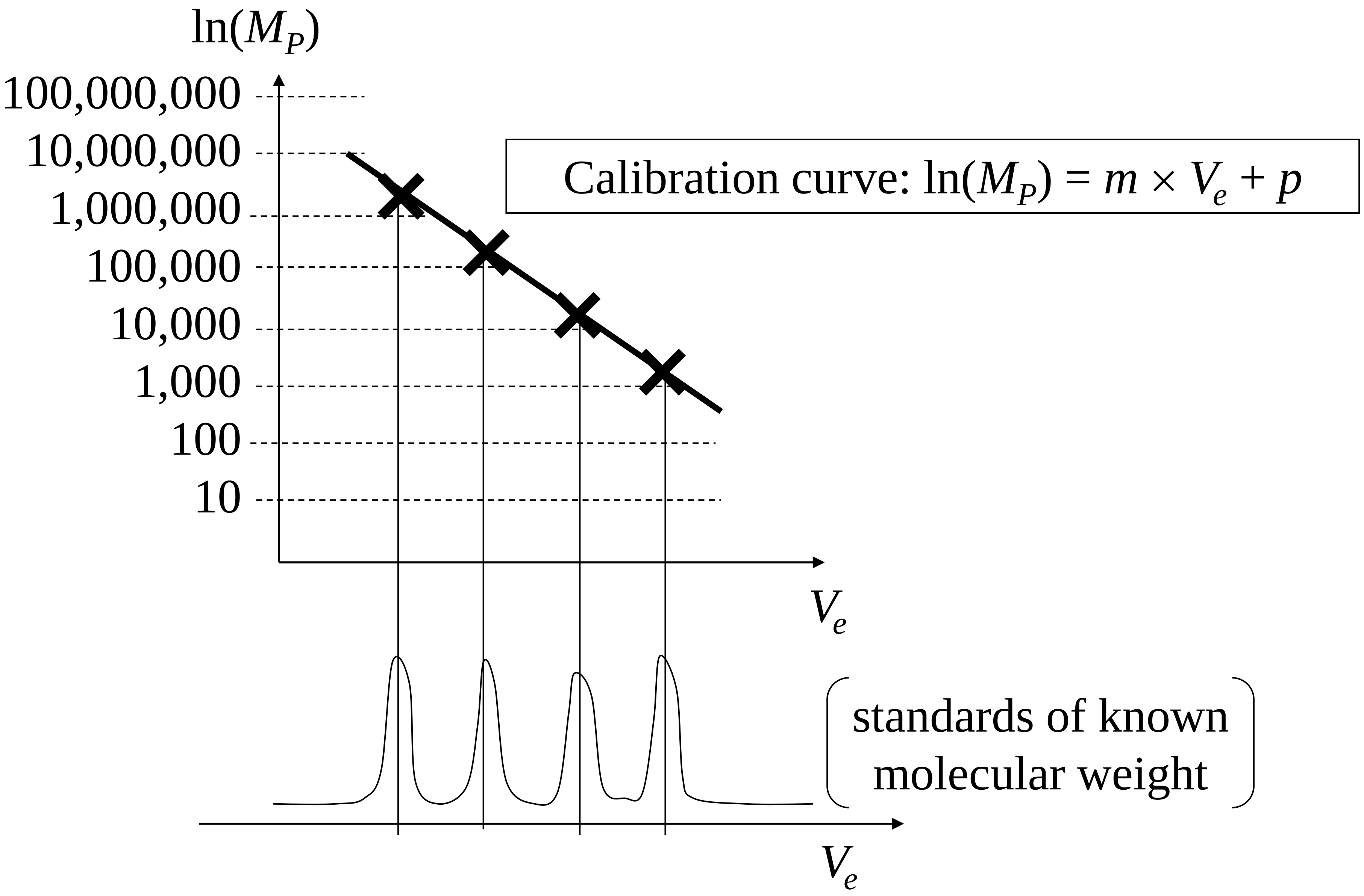




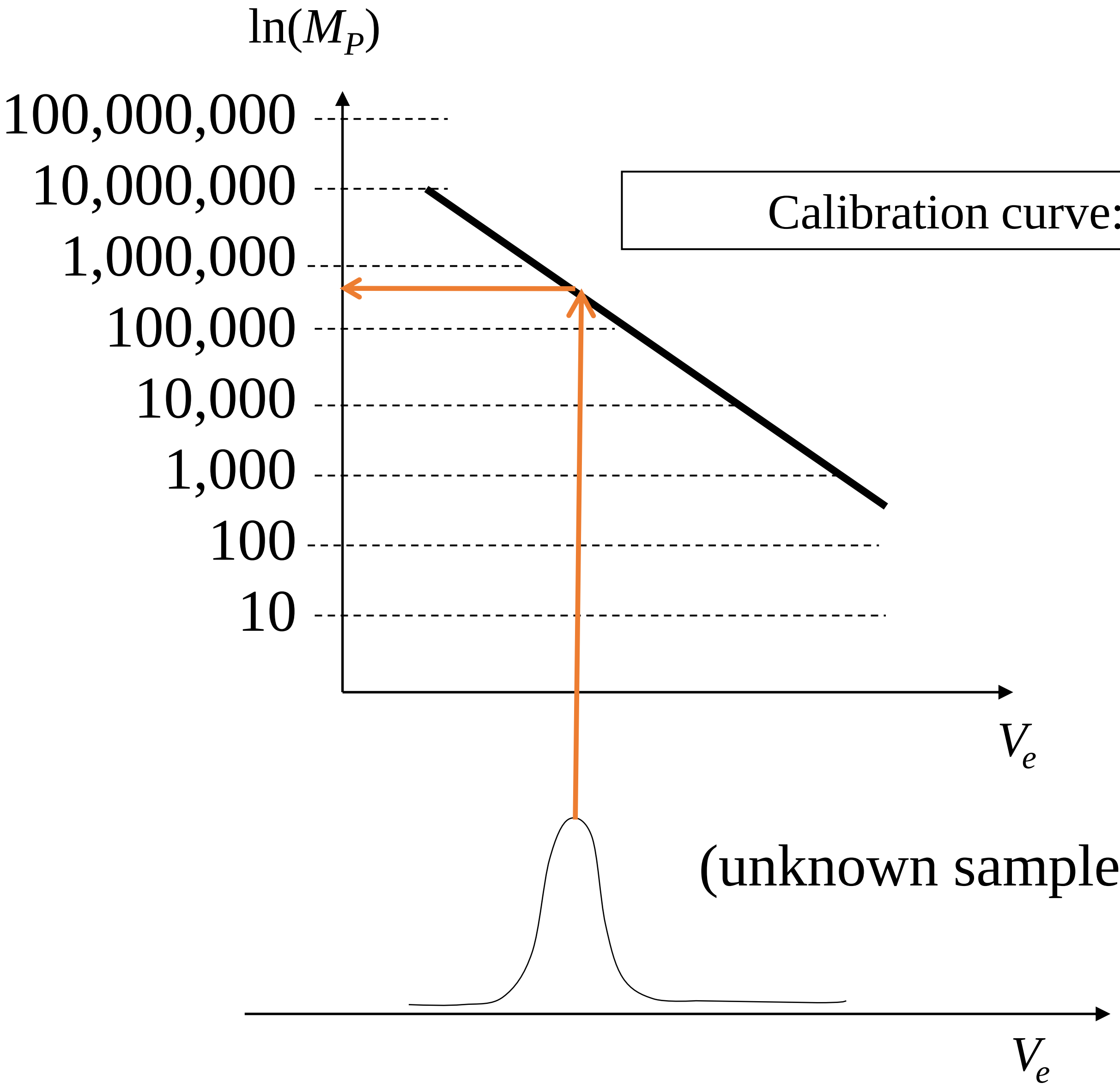
The calibration of the GPC column is done with monodisperse polymer **standards** (PDI~1) of known molecular weight.



Gel Permeation Chromatography (GPC) - Calibration:



Gel Permeation Chromatography (GPC) - Calibration:

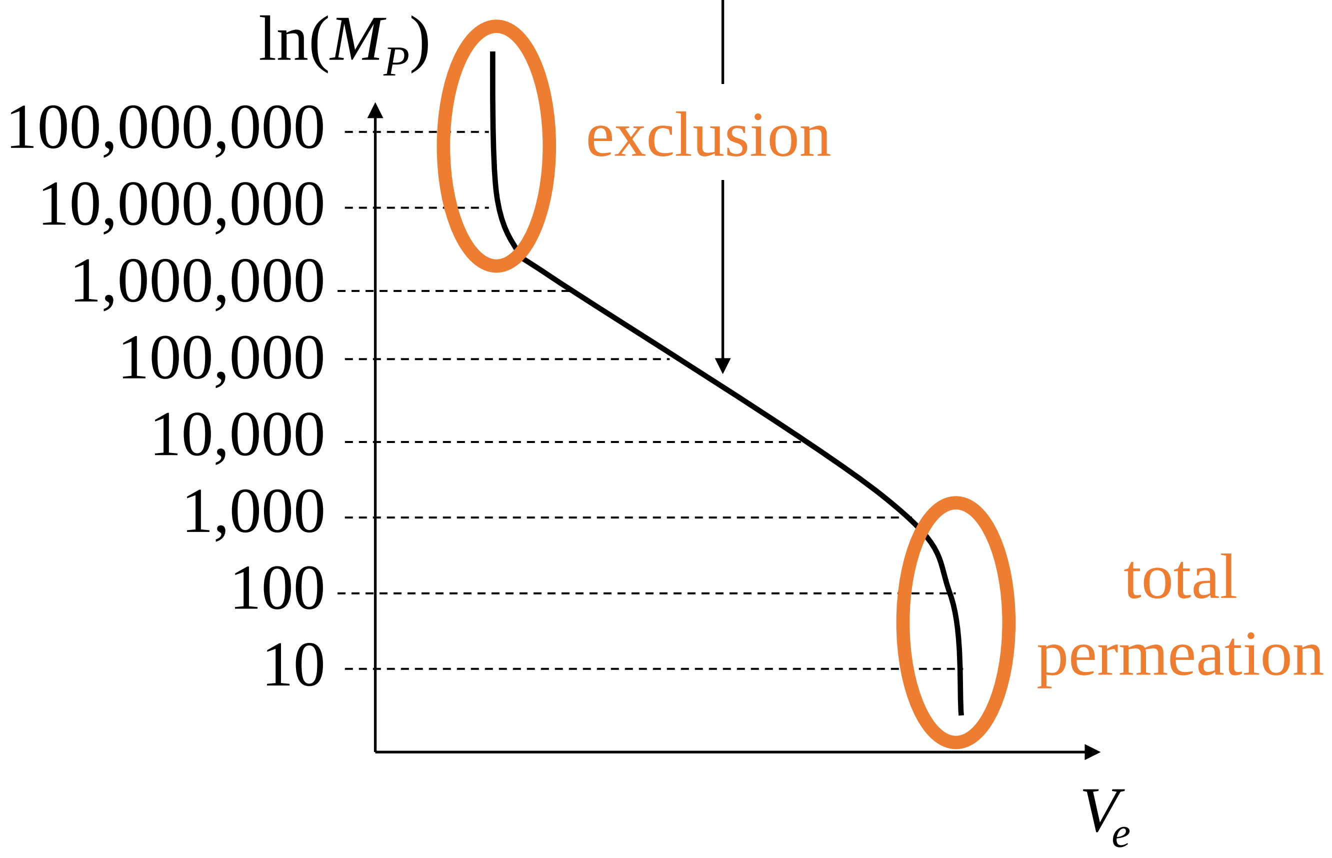


Calibration curve: $\ln(M_P) = m \times V_e + p$

(unknown sample)

Gel Permeation Chromatography (GPC):

Calibration curve: $\ln(M_P) = m \times V_e + p$



Detector: Differential Refractive Index (DRI)

DRI detector depends on the mass concentration:

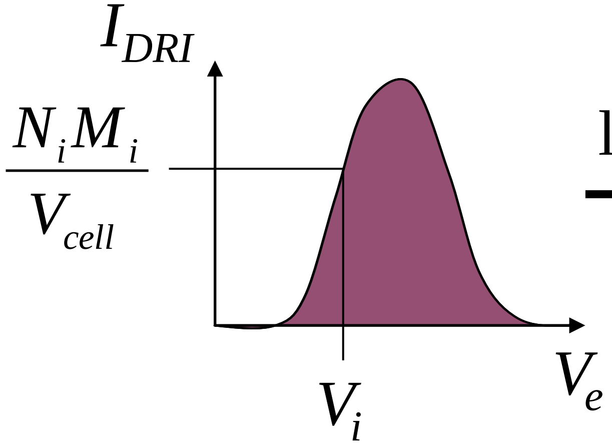
$$C_m = \frac{N \times M_P}{V_{cell}}$$ (V_{cell} = volume of the DRI detection cell)

V_{cell} = 8 µL, very small, so C_m = N x M_p

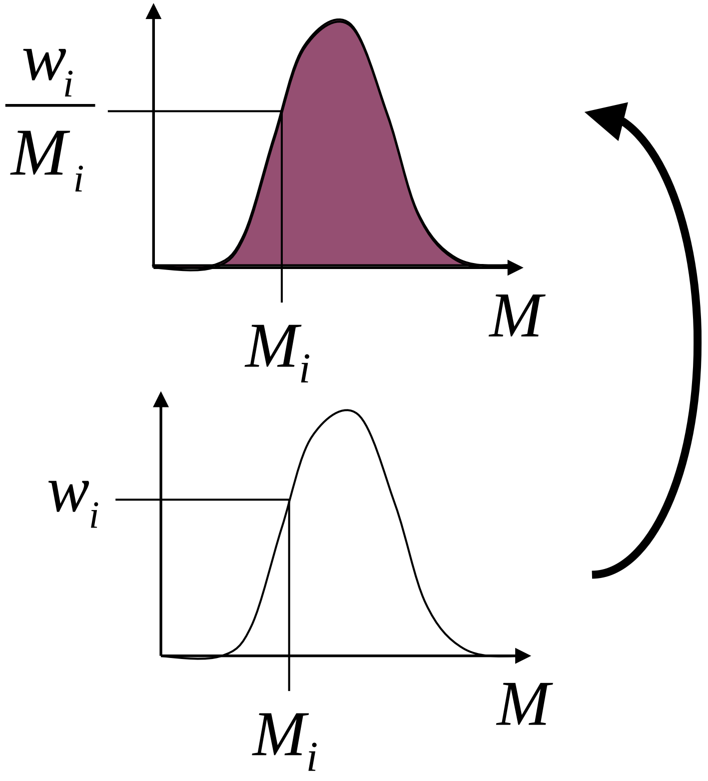
Gel Permeation Chromatography (GPC) –*Mn*:

$$Int\#1 = \sum \frac{w_i}{M_i} = \sum \frac{\frac{N_i M_i}{\sum N_i M_i}}{M_i} = \frac{1}{\sum N_i M_i} \sum \frac{N_i M_i}{M_i} = \frac{\sum N_i}{\sum N_i M_i}$$

$$\boxed{Int\#1 = M_n^{-1}}$$



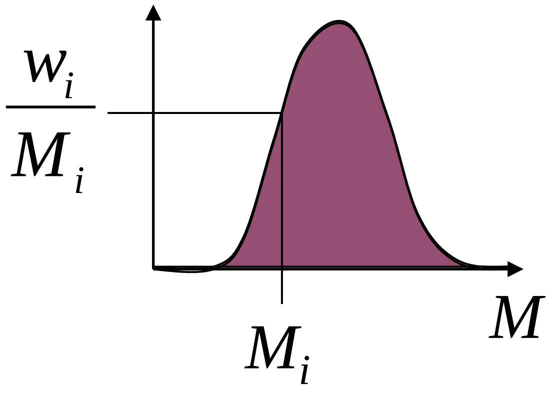
$$\ln(M_P) = m \times V_e + p$$



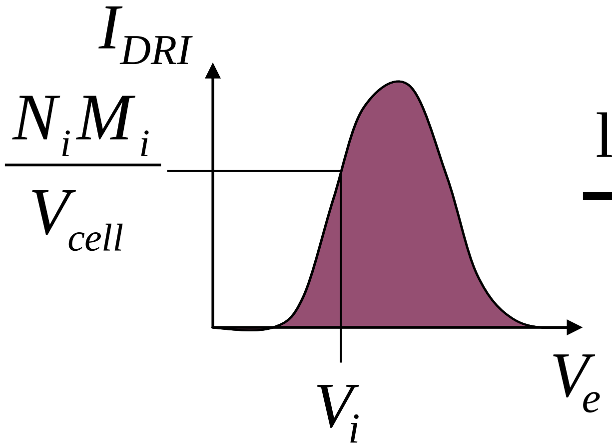
$$\frac{I_{DRI}}{\sum I_{DRI}} = \frac{N_i M_i / V_{cell}}{\sum N_i M_i / V_{cell}} = \frac{N_i M_i}{\sum N_i M_i} = w_i$$

Gel Permeation Chromatography (GPC) – *Mw* and PDI:

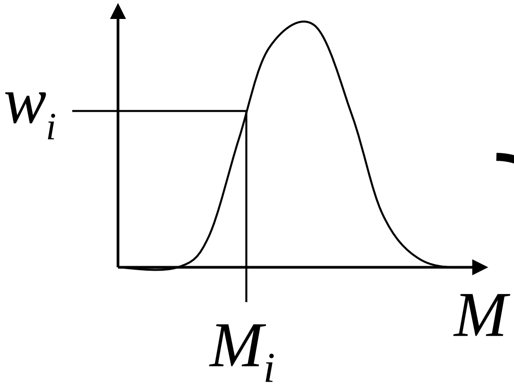
$$Int\#1 = \sum \frac{w_i}{M_i} = \sum \frac{\frac{N_i M_i}{\sum N_i M_i}}{M_i} = \frac{1}{\sum N_i M_i} \sum \frac{N_i M_i}{M_i} = \frac{\sum N_i}{\sum N_i M_i}$$



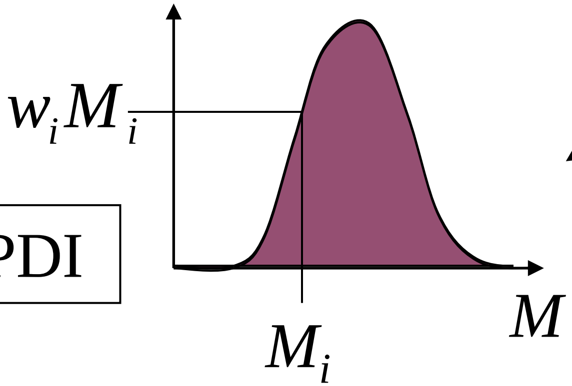
$$\boxed{Int\#1 = M_n^{-1}}$$



$$\ln(M_P) = m \times V_e + p$$



$$Int\#2 = \sum w_i M_i = \sum \frac{N_i M_i}{\sum N_i M_i} \times M_i = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$



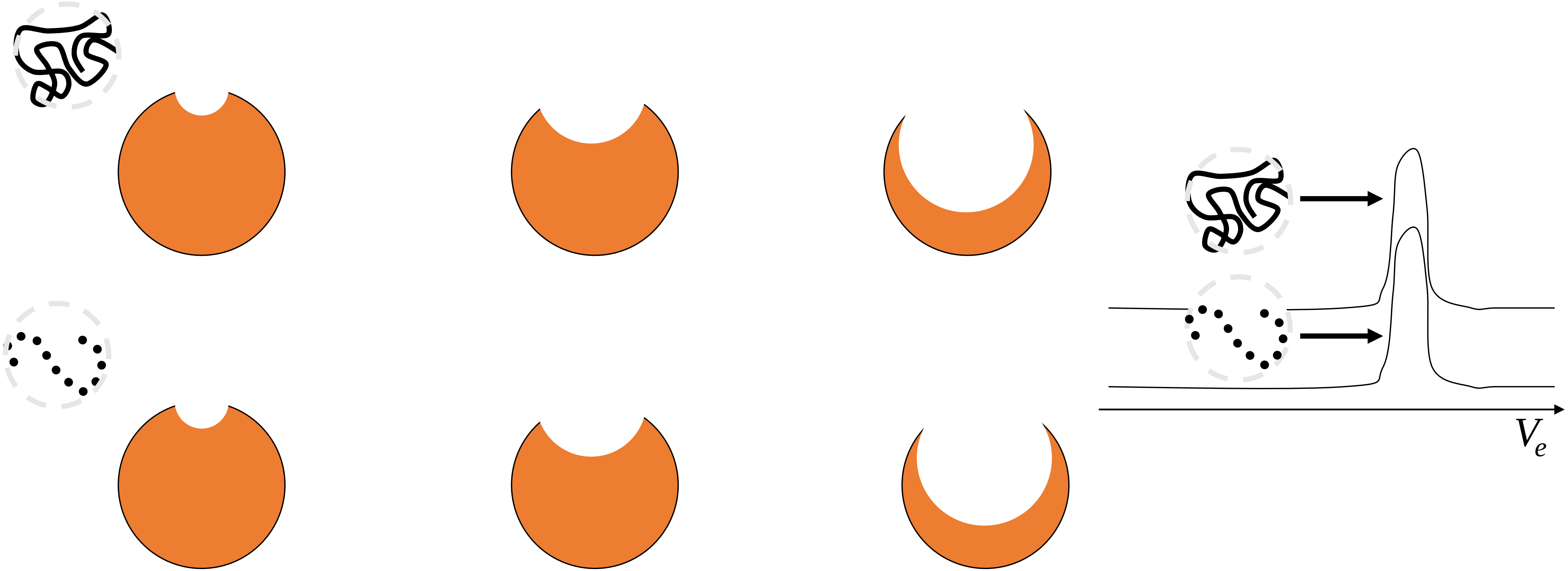
$$\boxed{Int\#2 = M_w} \qquad \boxed{Int\#1 \times Int\#2 = M_w/M_n = \text{PDI}}$$

Gel Permeation Chromatography (GPC) – Limitations:

- The calibration curve is only valid for the same type of polymer used for the calibration, under the same conditions (solvent, temperature, column).
- Narrow molecular weight distributions are only available for a limited number of polymers. Nevertheless, "apparent" molecular weights based on a polystyrene calibration curve are routinely reported in the literature.

7.3.2 Universal calibration curve – calibration with standards of different polymer

Two different polymers with the same hydrodynamic volume elute at the same elution volume.



Gel Permeation Chromatography (GPC) – Universal Calibration:

$$[\eta] = 2.5 \times N_A \times \frac{V_h}{M_P}$$

$$[\eta] \times M_P = 2.5 \times N_A \times V_h$$

According to the Mark-Houwink-Sakurada equation:

$[\eta] = K \times M_P^a$ with $0.5 < a < 0.8$

$$\boxed{[\eta] \times M_P = K \times M_P^{a+1} = 2.5 \times N_A \times V_h}$$

Gel Permeation Chromatography (GPC) – Universal Calibration:

$$\boxed{[\eta]\times M_P = K\times M_P^{a+1} = 2.5\times N_A\times V_h}$$

Two different polymers *A* and *B* eluting with the same elution volume have the same hydrodynamic volume V_h so that:

$$K_A M_{PA}^{a_A+1} = 2.5\times N_A\times V_h(A\,or\,B) = K_B M_{PB}^{a_B+1}$$

$$M_{PB} = \left(\frac{K_A}{K_B}\right)^{\frac{1}{a_B+1}} M_{PA}^{\frac{a_A+1}{a_B+1}}$$

A, B with known α and K

constants

$$Ln(M_{PB}) = \frac{1}{a_B+1}Ln\left(\frac{K_A}{K_B}\right) + \frac{a_A+1}{a_B+1}Ln(M_{PA})$$

Gel Permeation Chromatography (GPC) – Universal Calibration:

constants

$$Ln(M_{PB}) = \frac{1}{a_B+1} Ln\left(\frac{K_A}{K_B}\right) + \frac{a_A+1}{a_B+1} Ln(M_{PA})$$

If the column has been calibrated with polymer *A*, then we have:

$$Ln(M_{PA}) = m \times V_e + p$$

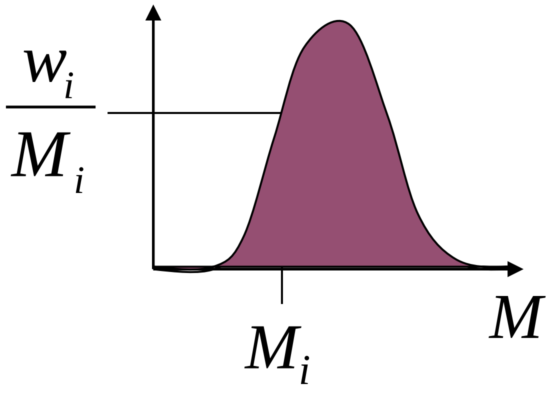
$$Ln(M_{PB}) = \left[\frac{1}{a_B+1} Ln\left(\frac{K_A}{K_B}\right) + \frac{a_B+1}{a_A+1} \times p\right] + \frac{a_A+1}{a_B+1} \times m \times V_e$$

constant = *p'*   **constant = *m'***

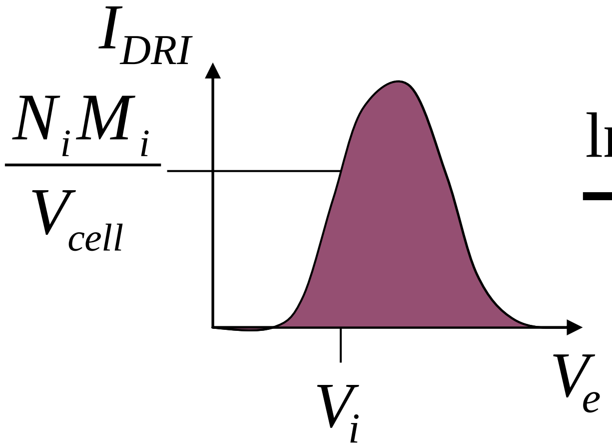
$$\boxed{Ln(M_{PB}) = m' \times V_e + p'}$$

Gel Permeation Chromatography (GPC) – *Mn*, *Mw*, and PDI:

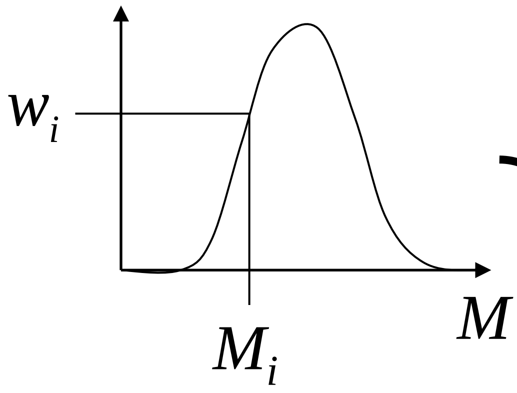
$$Int\#1=\sum\frac{w_i}{M_i}=\sum\frac{\frac{N_iM_i}{\sum N_iM_i}}{M_i}=\frac{1}{\sum N_iM_i}\sum\frac{N_iM_i}{M_i}=\frac{\sum N_i}{\sum N_iM_i}$$



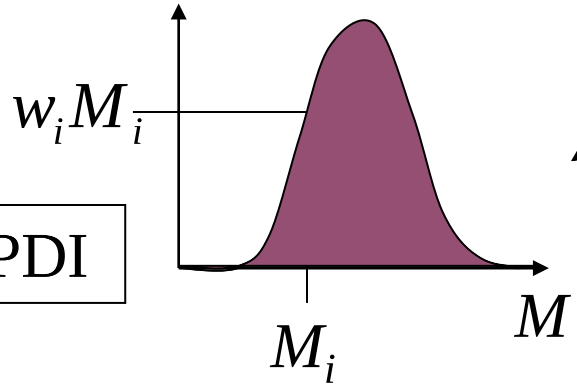
$$\boxed{Int\#1 = M_n^{-1}}$$



$$\ln(M_{PA}) = m \times V_e + p$$



$$Int\#2=\sum w_iM_i=\sum\frac{N_iM_i}{\sum N_iM_i}\times M_i=\frac{\sum N_iM_i^2}{\sum N_iM_i}$$

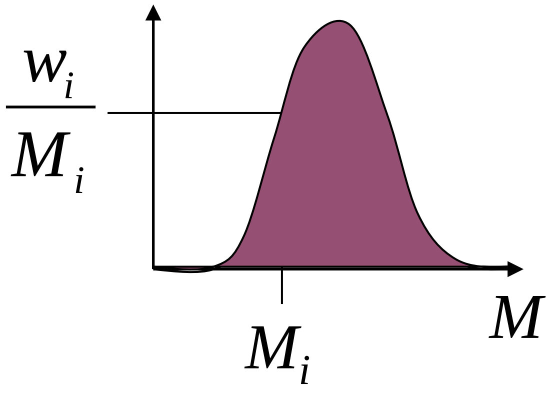


$$\boxed{Int\#2 = M_w}$$

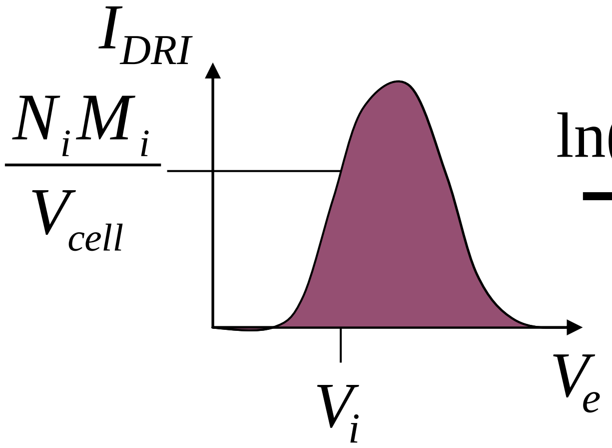
$$\boxed{Int\#1 \times Int\#2 = M_w/M_n = \text{PDI}}$$

Gel Permeation Chromatography (GPC) – *Mn*, *Mw*, and PDI:

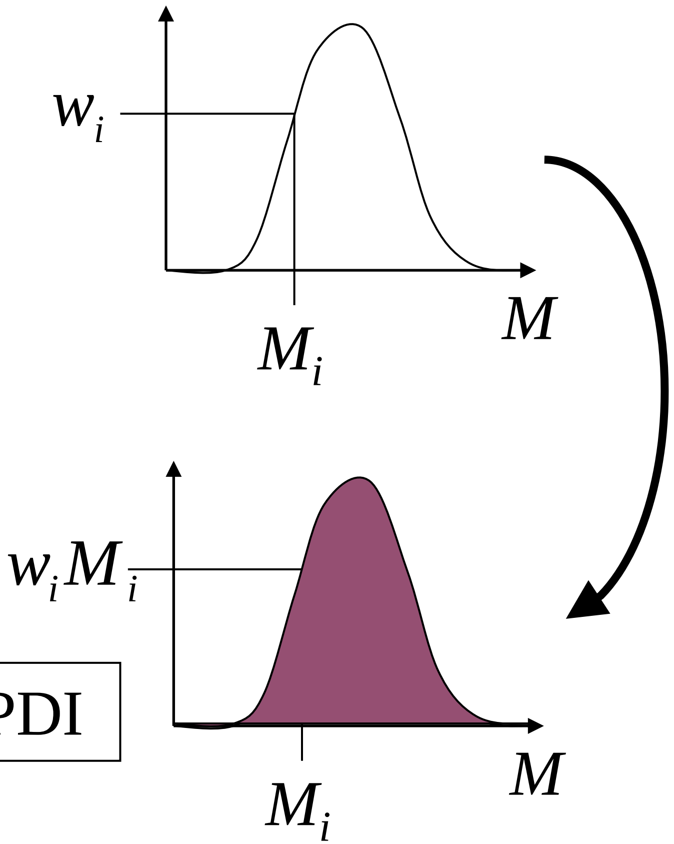
$$Int\#1 = \sum \frac{w_i}{M_i} = \sum \frac{\frac{N_iM_i}{\sum N_iM_i}}{M_i} = \frac{1}{\sum N_iM_i}\sum \frac{N_iM_i}{M_i} = \frac{\sum N_i}{\sum N_iM_i}$$



$$\boxed{Int\#1 = M_n^{-1}}$$



$$\ln(M_{PB}) = m' \times V_e + p'$$



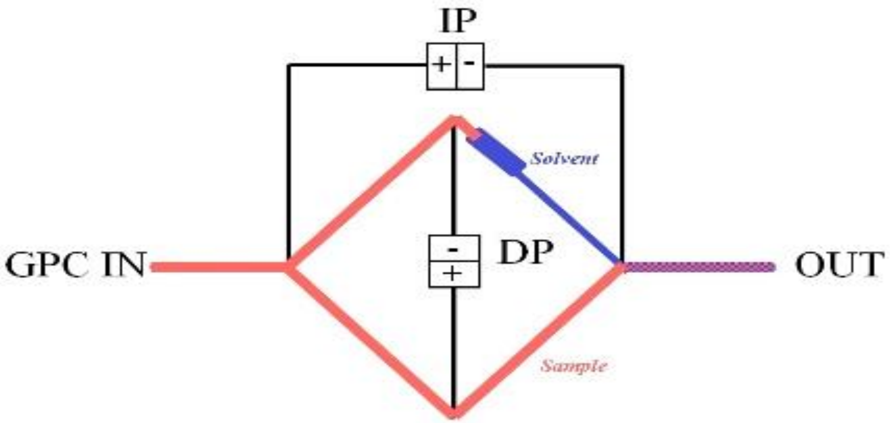
$$Int\#2 = \sum w_iM_i = \sum \frac{N_iM_i}{\sum N_iM_i} \times M_i = \frac{\sum N_iM_i^2}{\sum N_iM_i}$$

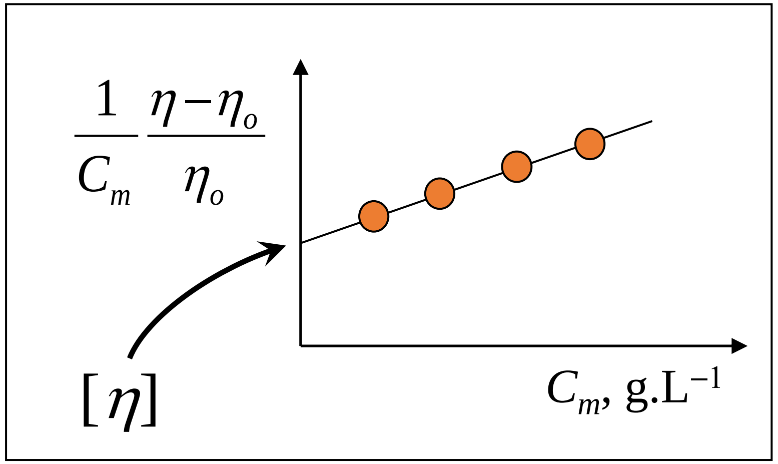
$$\boxed{Int\#2 = M_w} \qquad \boxed{Int\#1 \times Int\#2 = M_w/M_n = \text{PDI}}$$

If the α and K for B is unknown, *m’* and *p’* are not available for the calibration

$$\boxed{\ln(M_{PB}) = m' \times V_e + p'}$$

Viscosity detector





The concentration of the sample in the cell is very low

So $$[\eta] = \frac{1}{C_m}\frac{\eta-\eta_o}{\eta_o}$$

Gel Permeation Chromatography (GPC) – Universal Calibration:

$$\boxed{[\eta]\times M_P = K\times M_P^{a+1} = 2.5\times N_A\times V_h}$$

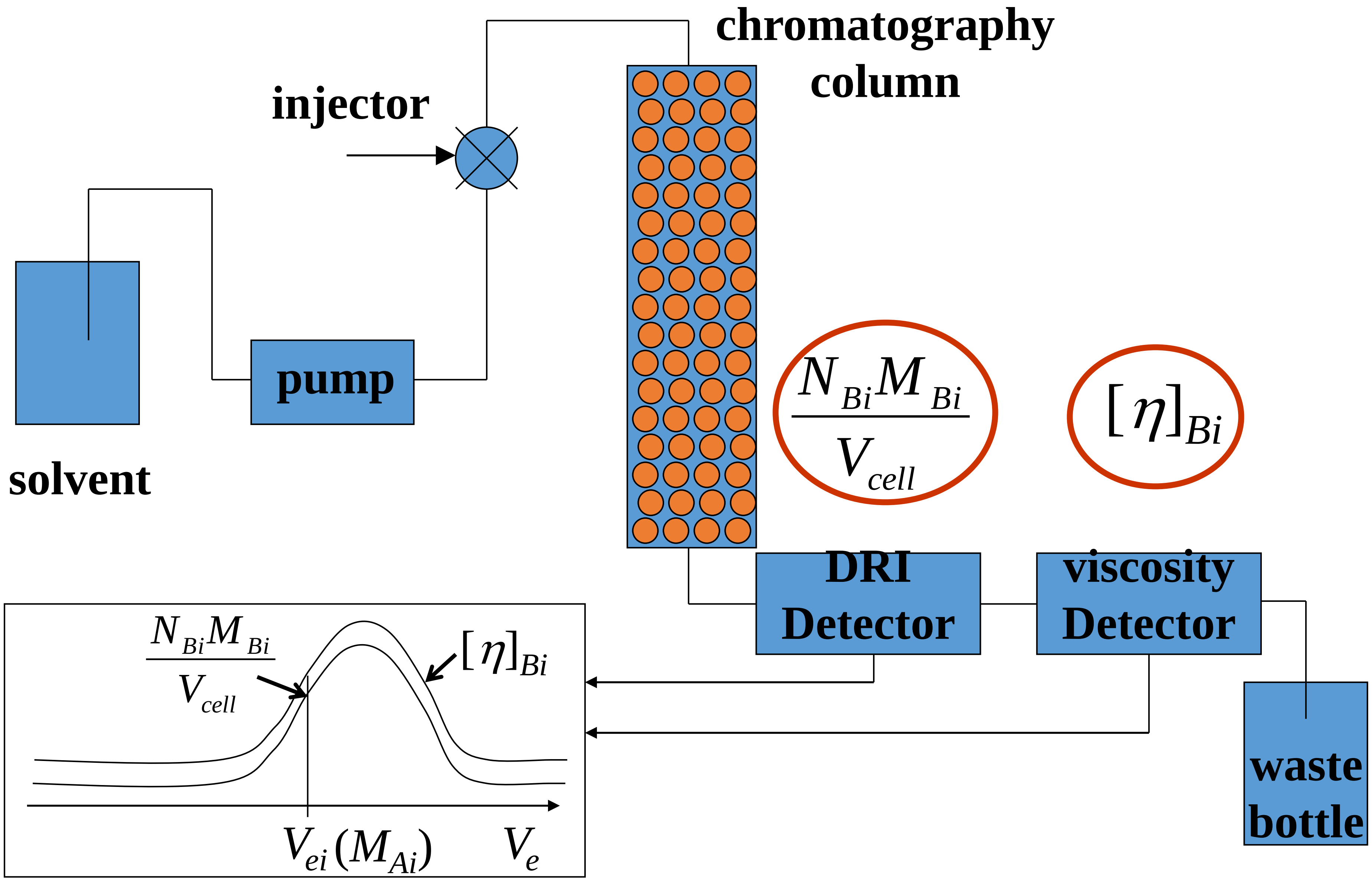
Two different polymers *A* and *B* eluting with the same elution volume have the same hydrodynamic volume V_h so that:

$$[\eta]_B M_{PB} = 2.5\times N_A\times V_h(A\,or\,B) = K_A M_{PA}^{a_A+1}$$

experimentally known quantities

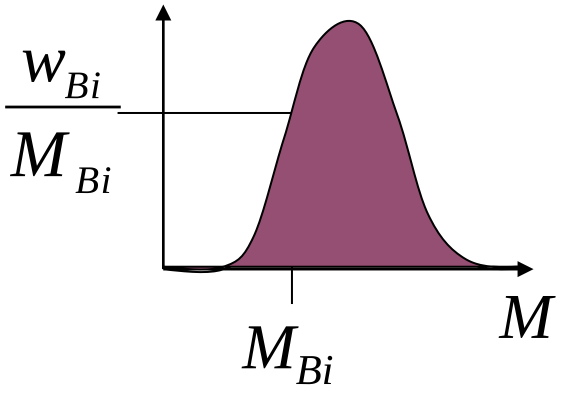
$$\boxed{M_{PB} = \frac{K_A M_{PA}^{a_A+1}}{[\eta]_B}}$$

Gel Permeation Chromatography (GPC) – Universal Calibration:

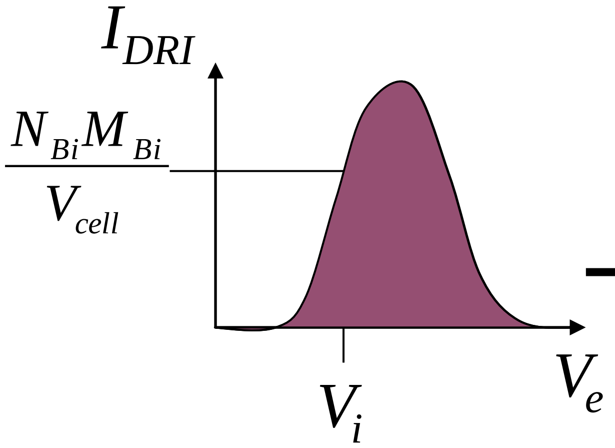


Gel Permeation Chromatography (GPC) – *Mn*, *Mw*, and PDI:

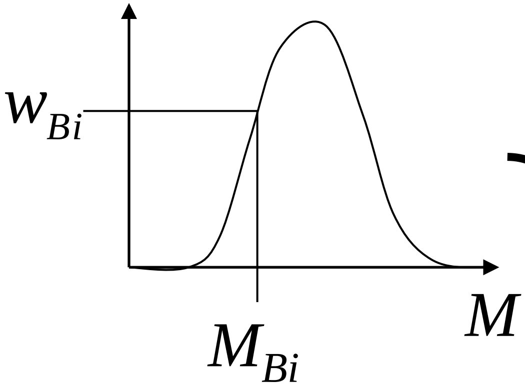
$$Int\#1 = \sum \frac{w_i}{M_i} = \sum \frac{\dfrac{N_i M_i}{\sum N_i M_i}}{M_i} = \frac{1}{\sum N_i M_i} \sum \frac{N_i M_i}{M_i} = \frac{\sum N_i}{\sum N_i M_i}$$



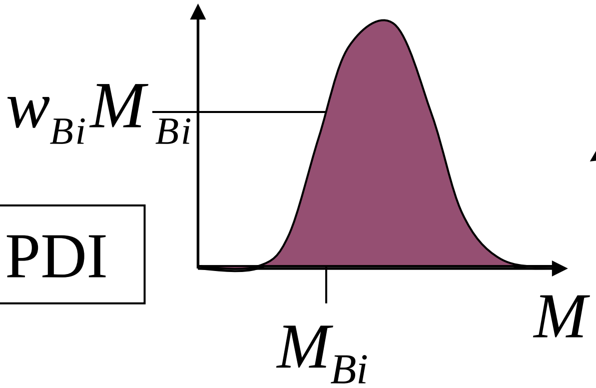
$$\boxed{Int\#1 = M_n^{-1}}$$



$$M_{Bi} = \frac{K_A M_{PA}^{a_A+1}}{[\eta]_{Bi}}$$



$$Int\#2 = \sum w_i M_i = \sum \frac{N_i M_i}{\sum N_i M_i} \times M_i = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

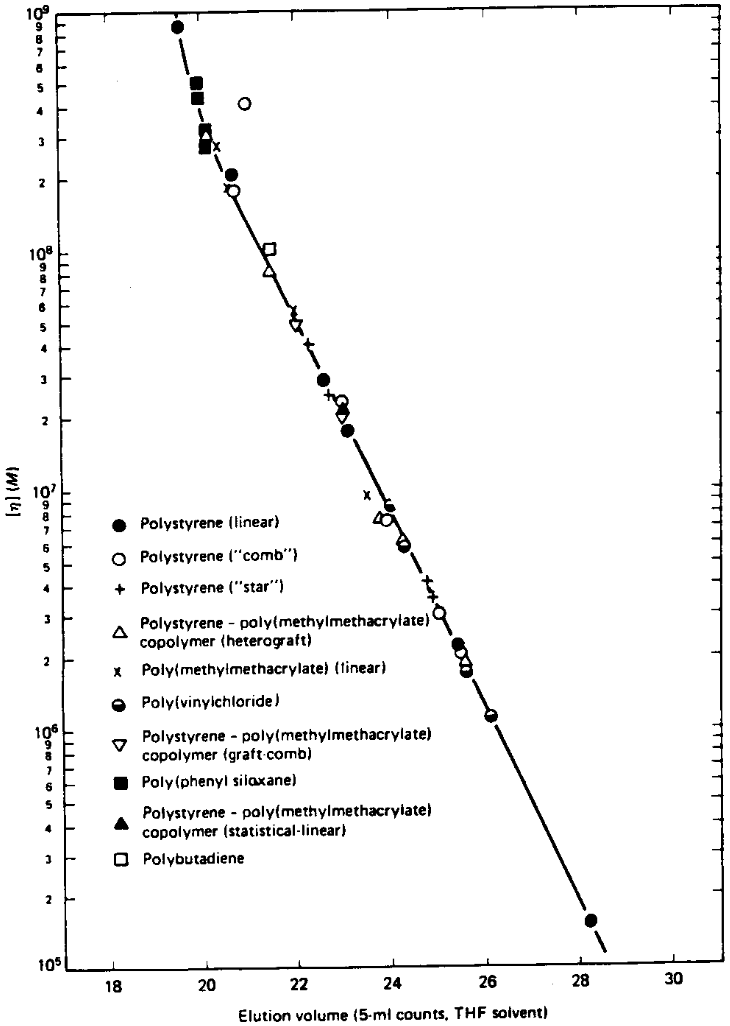


$$\boxed{Int\#2 = M_w} \qquad \boxed{Int\#1 \times Int\#2 = M_w/M_n = \text{PDI}}$$

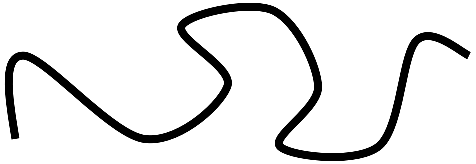
Gel Permeation Chromatography (GPC) – Universal Calibration:

Benoit et al. *Polym. Lett.* **1967**, *5*, 753

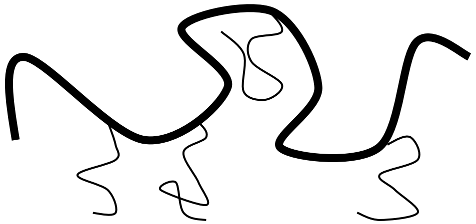
$[\eta] \times M_P$



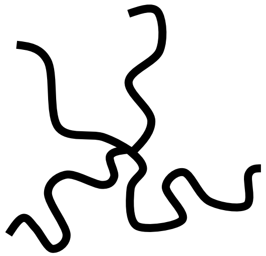
linear



comb



star



The molecular weight of a new polymer can be measured by GPC using universal calibration; but the sample has to be prepared with an accurate concentration.

Summary / Review

- Gel permeation chromatography separates chains by hydrodynamic volume
  - Only method to produce entire molecular weight distribution (MWD) curve
- Calibration curve correlates elution volume and molecular weight peak (Mp)
- Refractive index and viscometer most popular detectors
- Universal calibration curve allows measurement of MWD curve using calibration made with a different polymer (when α and K are known)

Summary of Methods:

Ebullioscopy and cryoscopy: M_n < 30,000 g.mol^{-1}, yields M_n.

Vapor pressure depression: M_n < 20,000 g.mol^{-1}, yields M_n.

Membrane osmometry: any M_n.

End group analysis: M_n < 1,000,000 g.mol^{-1}, yields M_n; depends on the efficiency of the labeling reaction.

Light scattering: any M_n, yields M_w.

Viscometry: any M_n, yields $M_v \approx M_w$

Gel permeation chromatography: M_n < 10,000,000 g.mol^{-1}, yields M_n, M_w, PDI, and the entire distribution.