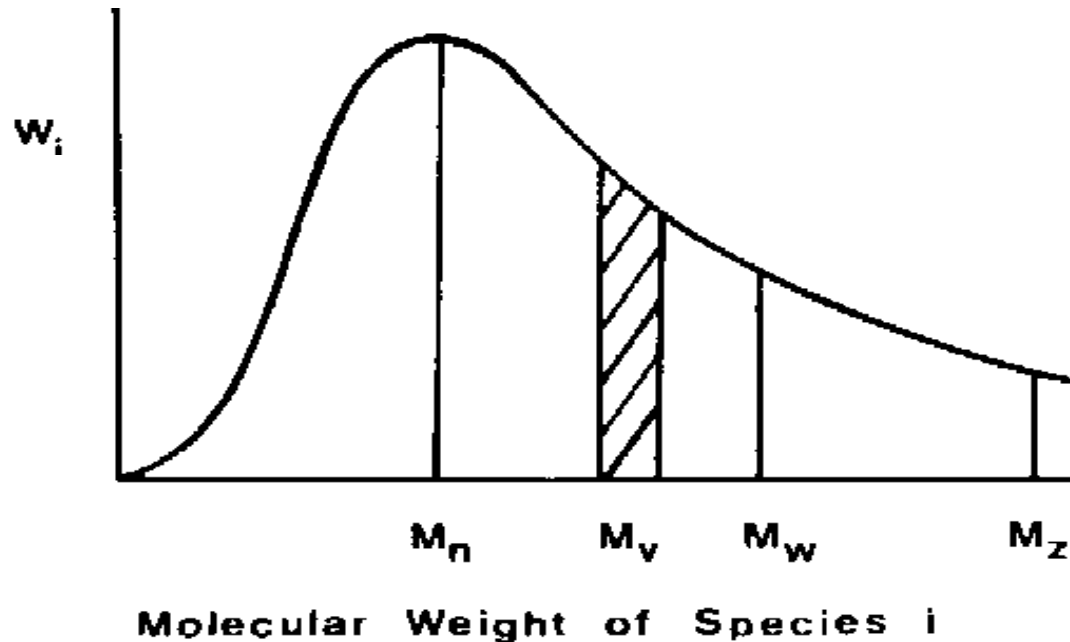


# Determination of the molecular weight of polymers

- Unlike small molecules, polymers are typically a mixture of differently sized molecules. Only an average molecular weight can be defined.



In case of Low MW,      Molecular Wt. =  $M = \frac{W}{N} = \frac{\text{total sample wt}}{\text{number of moles in sample}}$

**a. Absolute method:**

mass spectrometry, colligative property

end group analysis, light scattering, ultracentrifugation

**b. Relative method:** solution viscosity

**c. Fractionation method:** GPC

A. number average molecular weight ( $\overline{M}_n$ )

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i} \quad \text{(colligative property and end group analysis)}$$

B. weight average molecular weight ( $\overline{M}_w$ )

$$\overline{M}_w = \frac{\sum W_i M_i}{\sum W_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad \text{(light scattering)}$$

C. z average molecular weight ( $\overline{M}_z$ )

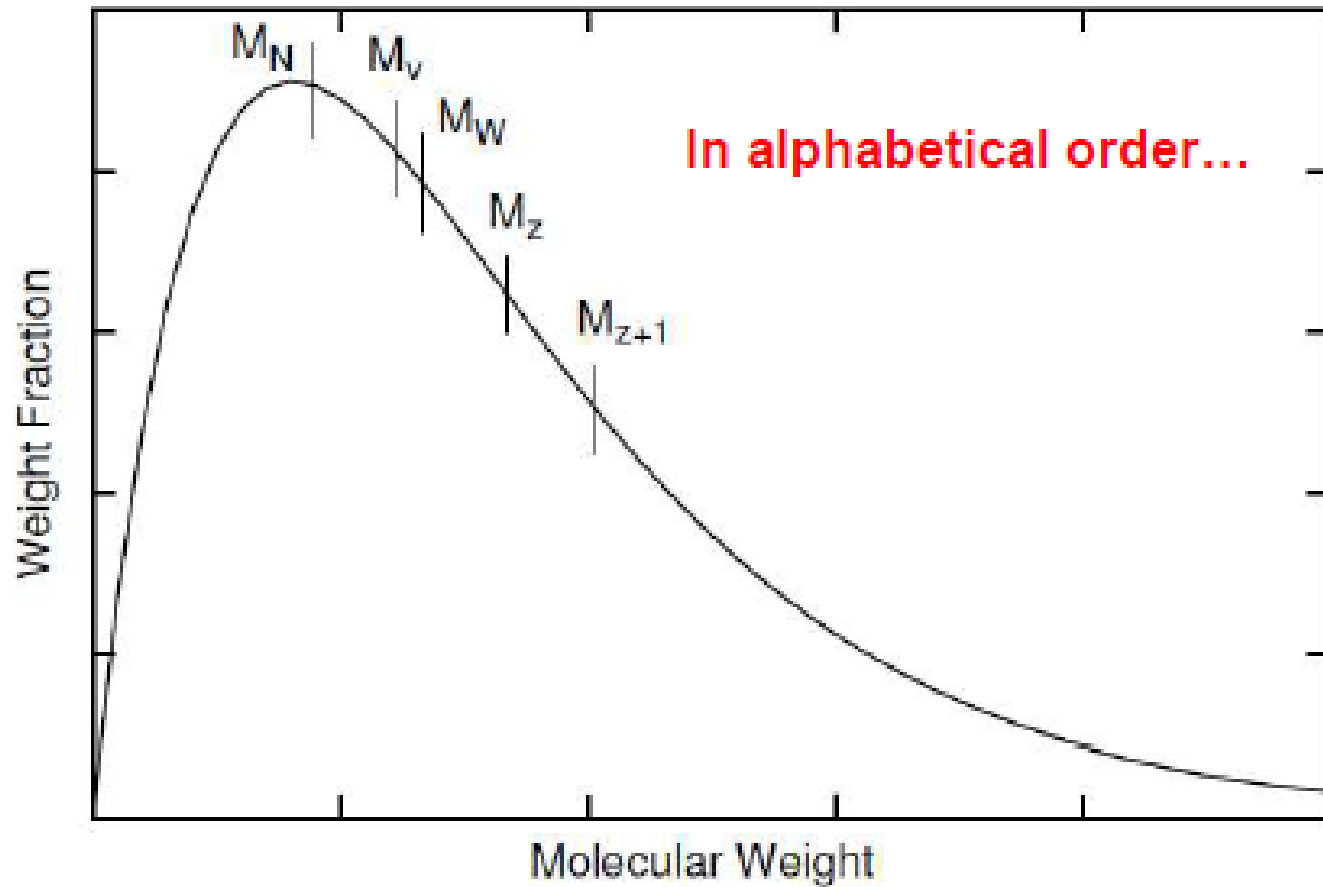
$$\overline{M}_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} \quad \text{(ultracentrifugation)}$$

D. general equation of average molecular weight :

$$\overline{M} = \frac{\sum N_i M_i^{a+1}}{\sum N_i M_i^a} \quad (\mathbf{a=0, \overline{M}_n \quad a=1, \overline{M}_w \quad a=2, \overline{M}_z})$$

E.  $\overline{M}_z > \overline{M}_w > \overline{M}_n$

# Average molecular weights



## Polydispersity index (PDI)

Measure of the distribution of molecular mass in a given polymer sample.

The PDI calculated is the weight average molecular weight divided by the number average molecular weight.

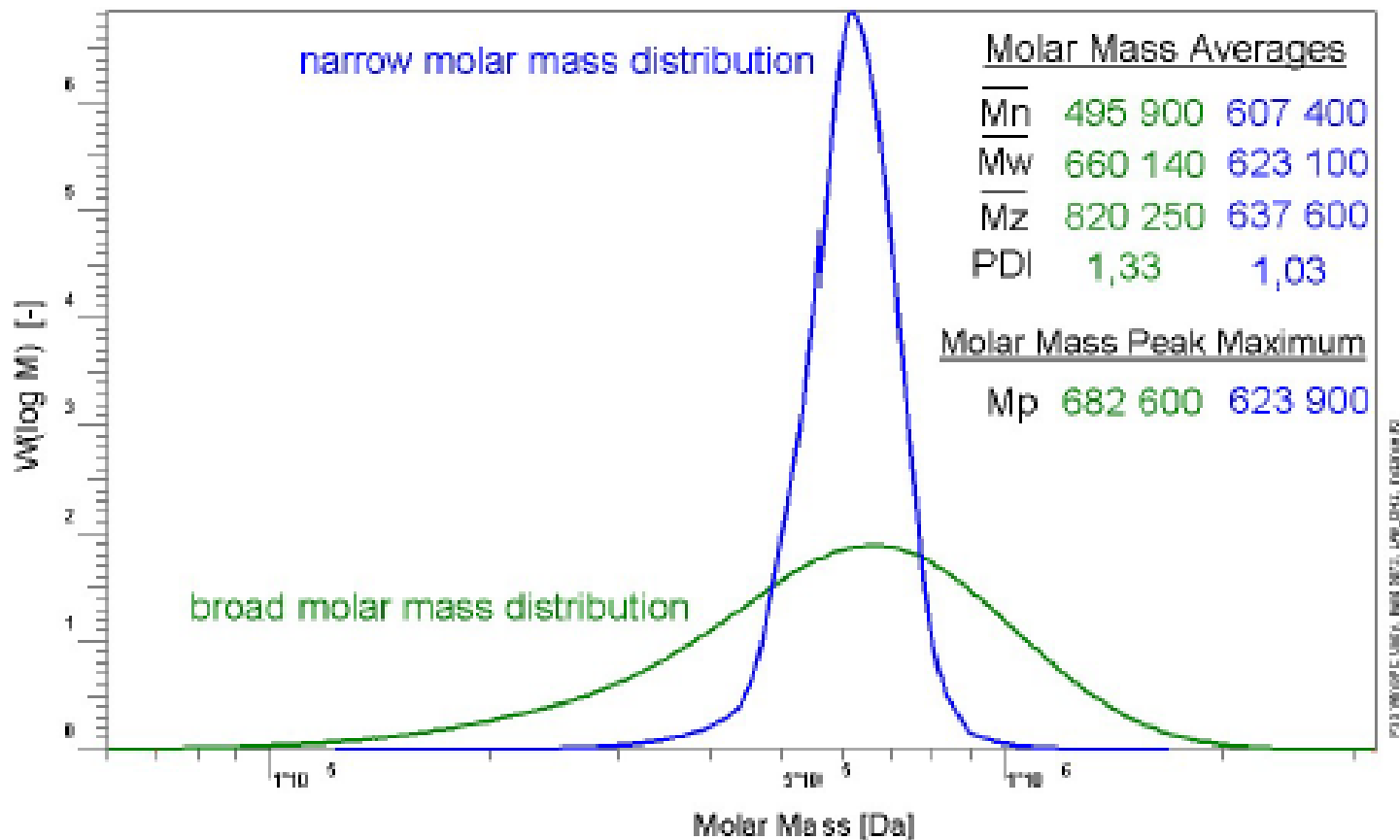
The PDI has a value always greater than 1,

But as the polymer chains approach uniform chain length, the PDI approaches unity (1).

$$\frac{\overline{M}_w}{\overline{M}_n} > 1 \quad \text{Polydisperse}$$

$$\frac{\overline{M}_w}{\overline{M}_n} = 1 \quad \text{Monodisperse}$$

# Molar mass distribution for a narrow and broad polystyrene (molar mass averages are also given)



# Determination of average molecular weights

- **Primary (absolute values) methods:**
  - Osmometry ( $M_n$ )
  - Scattering ( $M_w$ )
  - Sedimentation ( $M_z$ ) Z-average molecular weight is obtained from centrifugation data
- **Secondary (relevant to reference or calibration) methods:**
  - Gel permeation chromatography (GPC), also called size exclusion chromatography (SEC) to obtain molecular weight distribution
  - Intrinsic viscosity for determining viscosity average molecular weight

# Measurement of Number Average Molecular Weight

## 1. End-group Analysis

**A. Molecular weight limitation up to 50,000**

**B. End-group must have detectable species**

a. vinyl polymer :  $-\text{CH}=\text{CH}_2$

b. ester polymer :  $-\text{COOH}$ ,  $-\text{OH}$

c. amide and urethane polymer :  $-\text{NH}_2$ ,  $-\text{NCO}$

d. radioactive isotopes or UV, IR, NMR detectable functional group



## D. Requirement for end group analysis

1. The method cannot be applied to branched polymers
2. In a linear polymer there are twice as many end of the chain and groups as polymer molecules
3. If having different end group, the number of detected end group is average MW
4. End group analysis could be applied for polymerization mechanism identified

## E. High solution viscosity, low solubility, steric hindrance:

$$M_n = 5,000 \sim 10,000$$

$$\text{C. } \overline{M}_n = \frac{2 \times 1000 \times \text{sample wt}}{\text{meq COOH} + \text{meq OH}}$$

## 2. The measure of colligative property

**Colligative properties** are properties of solutions that depend on the number of particles in a given volume of solvent and not on the mass of the particles.

the freezing point depression, the boiling point elevation,  
the steam pressure depression, the osmotic pressure

→ **The mole number of polymer** → **average molecular weight**

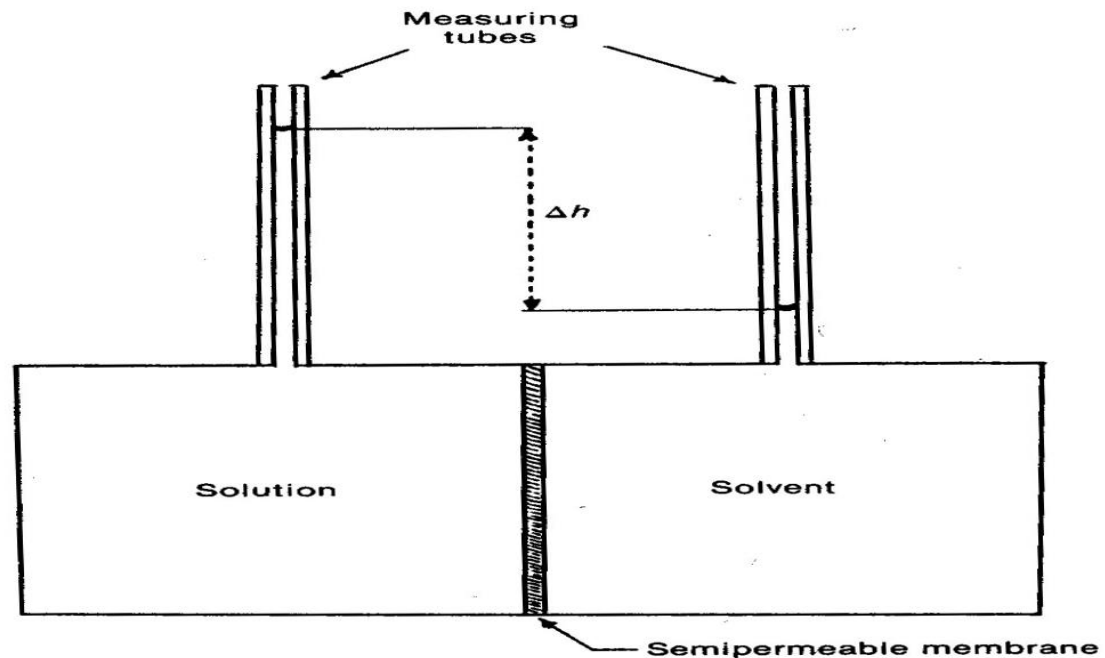
# (i) Membrane Osmometry

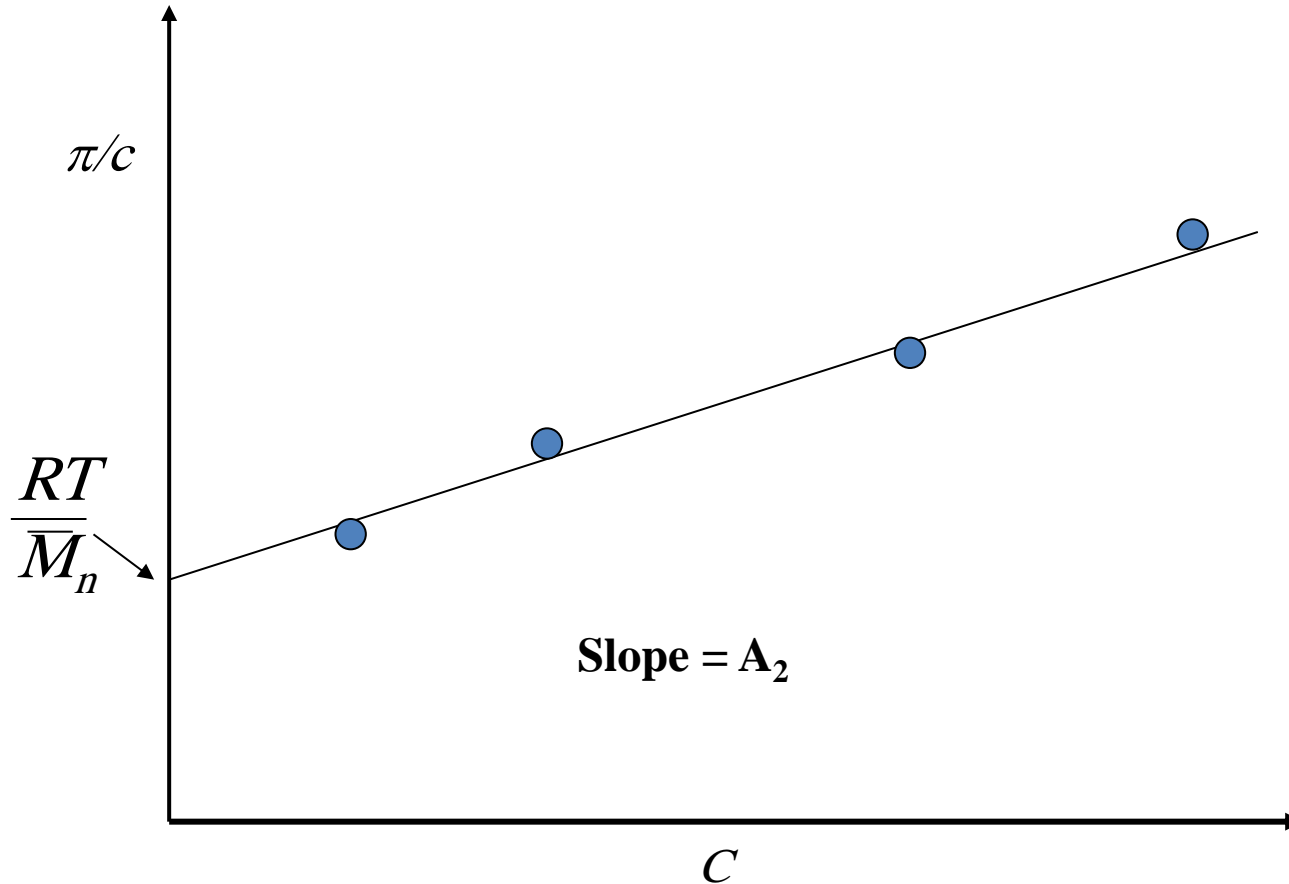
A. According to van't Hoff equation

$$\left(\frac{\pi}{c}\right)_{c=0} = \frac{RT}{M_n} + A_2C$$

limitation of : 50,000 ~ 2,000,000

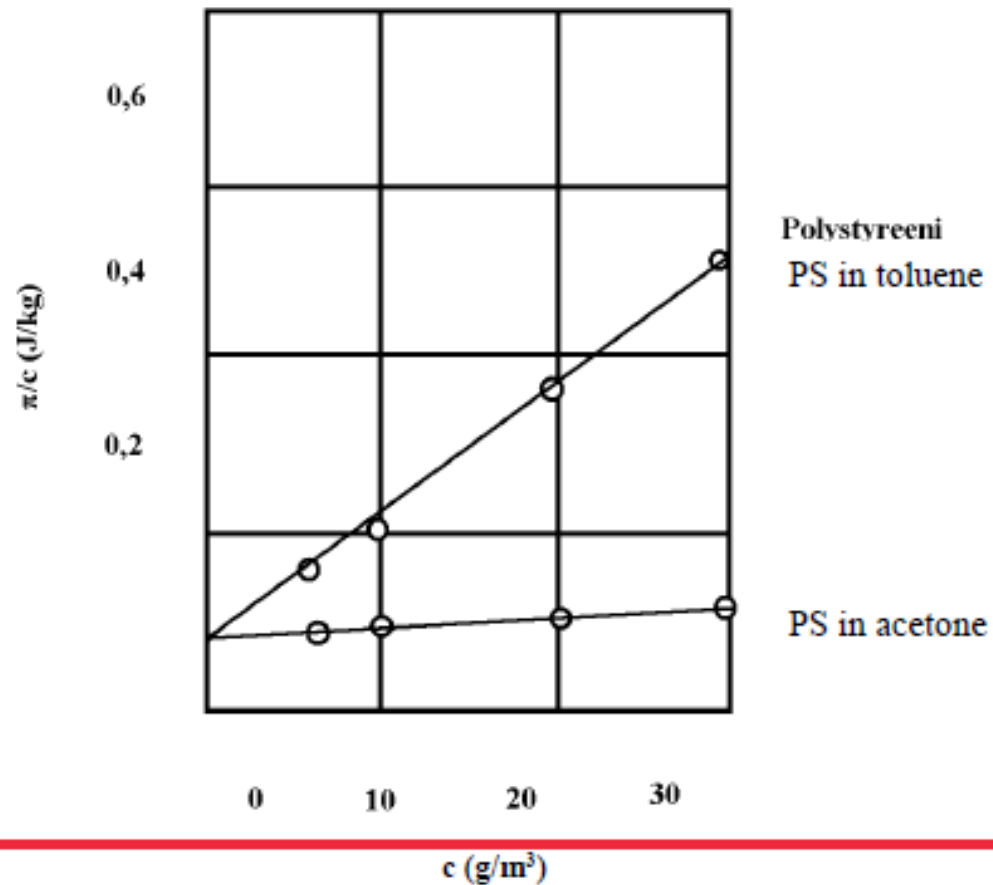
The major error arises from low-molecular-weight species diffusing through the membrane.





**Plot of reduced osmotic pressure ( $\pi/c$ ) versus concentration ( $c$ ).**

# Osmometric measurement: determining $\pi/c$



## (ii) Freezing-point depression (Cryoscopy)

$$\left(\frac{\Delta T_f}{C}\right)_{C=0} = \frac{RT^2}{\rho\Delta H_f \overline{M}_n} + A_2 C$$

$\Delta T_f$  : freezing-point depression,

$C$  : the concentration in grams per cubic centimeter

$R$  : gas constant

$T$  : freezing point

$\Delta H_f$ : the latent heats of fusion

$A_2$  : second virial coefficient

## (iii) Boiling-point elevation (Ebulliometry)

$$\left(\frac{\Delta T_b}{C}\right)_{C=0} = \frac{RT^2}{\rho\Delta H_v \overline{M}_n} + A_2 C$$

$\Delta T_b$  : boiling point elevation

$\Delta H_v$  : the latent heats of vaporization

- We use thermistor to major temperature. ( $1 \times 10^{-4}^\circ\text{C}$ )  
limitation of  $\overline{M}_n$  : below 20,000

## (iv) Vapor Pressure Osmometry

The measuring vapor pressure difference of solvent and solution drops.

$$\Delta T = \left( \frac{RT^2}{\lambda 100} \right) m$$

$\lambda$  : the heat of vaporization per gram of solvent  
m : molality

limitation of  $M_n$  : below 25,000

Calibration curve is needed to obtain molecular weight of polymer sample

Standard material : Benzil

# Viscometry

A. IUPAC suggested the terminology of solution viscosities as following.

Relative viscosity :

$$\eta_{rel} = \frac{\eta}{\eta_o} = \frac{t}{t_o}$$

$\eta$  : solution viscosity

$\eta_o$  : solvent viscosity

$t$  : flow time of solution

$t_o$  : flow time of solvent

Specific viscosity :

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = \frac{t - t_o}{t_o} = \eta_{rel} - 1$$

Reduced viscosity :

$$\eta_{rel} = \frac{\eta_{sp}}{c} = \frac{\eta_{rel} - 1}{c}$$

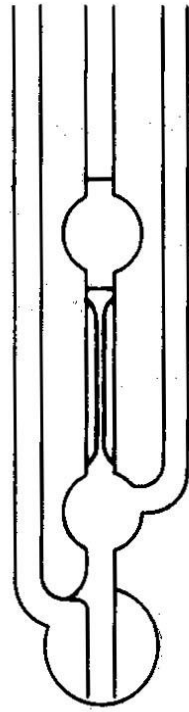
Inherent viscosity :

$$c \quad \eta_{inh} = \frac{\ln \eta_{rel}}{c}$$

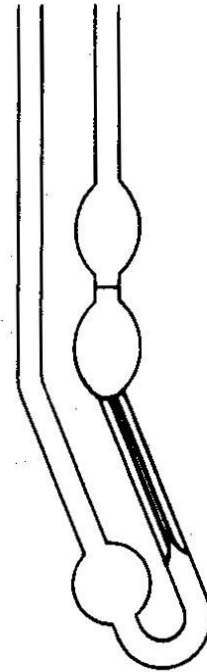
Intrinsic viscosity :

$$[\eta] = \left( \frac{\eta_{sp}}{c} \right)_{c=0} = (\eta_{inh})_{C=0}$$





**A**



**B**

**Capillary viscometers : (A) Ubbelohde, and (B) Cannon-Fenske.**

# Determination of Molecular Weight

## Viscosity Average Molecular Weight

### *Viscometry*

- The concentration dependence is observed to follow this functional dependence:

$$\frac{\eta_{sp}}{c} = [\eta] + k[\eta]^2 c + k'c^2$$

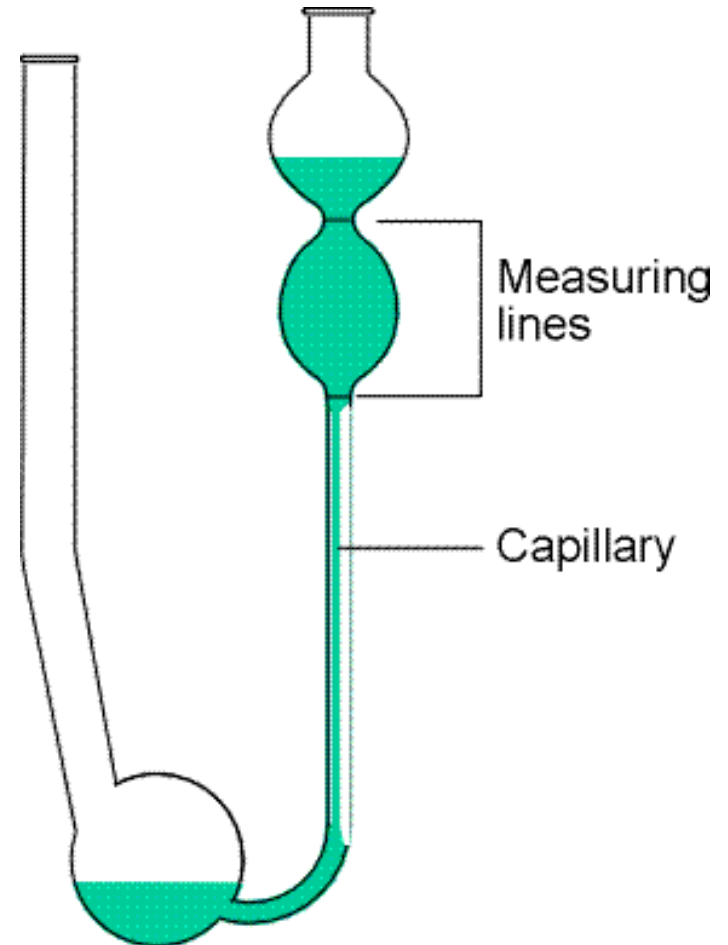
↑  
y-intercept

k = Huggins constant

k=2 for rigid uncharged spheres

k=0.35 for flexible polymers

- Neglect higher order term in c.
- Plot of  $\eta_{sp}/c$  vs c will yield [h] as y-intercept.



## Mark-Houwink-Sakurada equation

$$[\eta] = KM^a$$

$$\log[\eta] = \log K + a \log \overline{M}_v$$

- **K and a are empirical parameters characteristic of a polymer and a solvent**

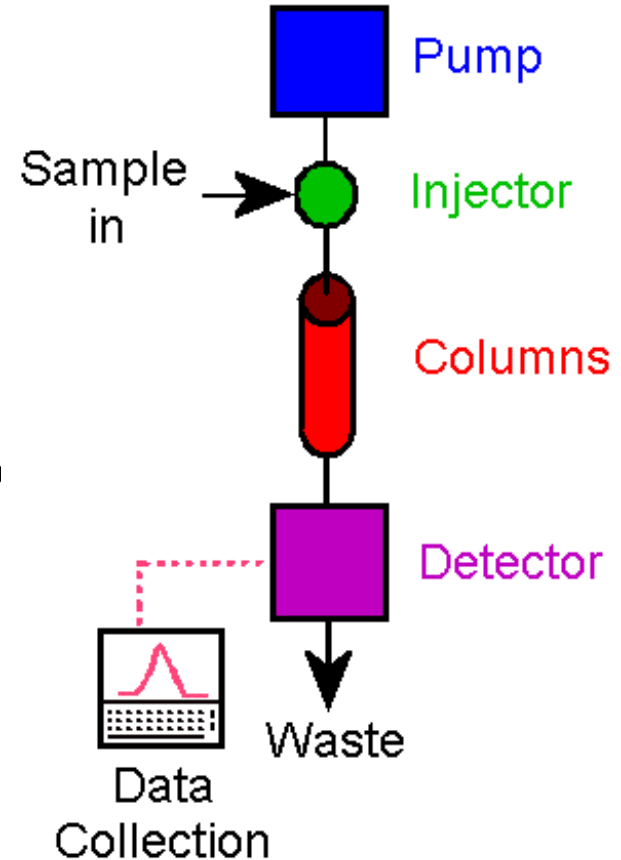
- a=0.5 for a well-coiled polymer in a poor solvent
- a=1.7 for rigid rod-like polymer

$$\overline{M}_w > \overline{M}_v > \overline{M}_n$$

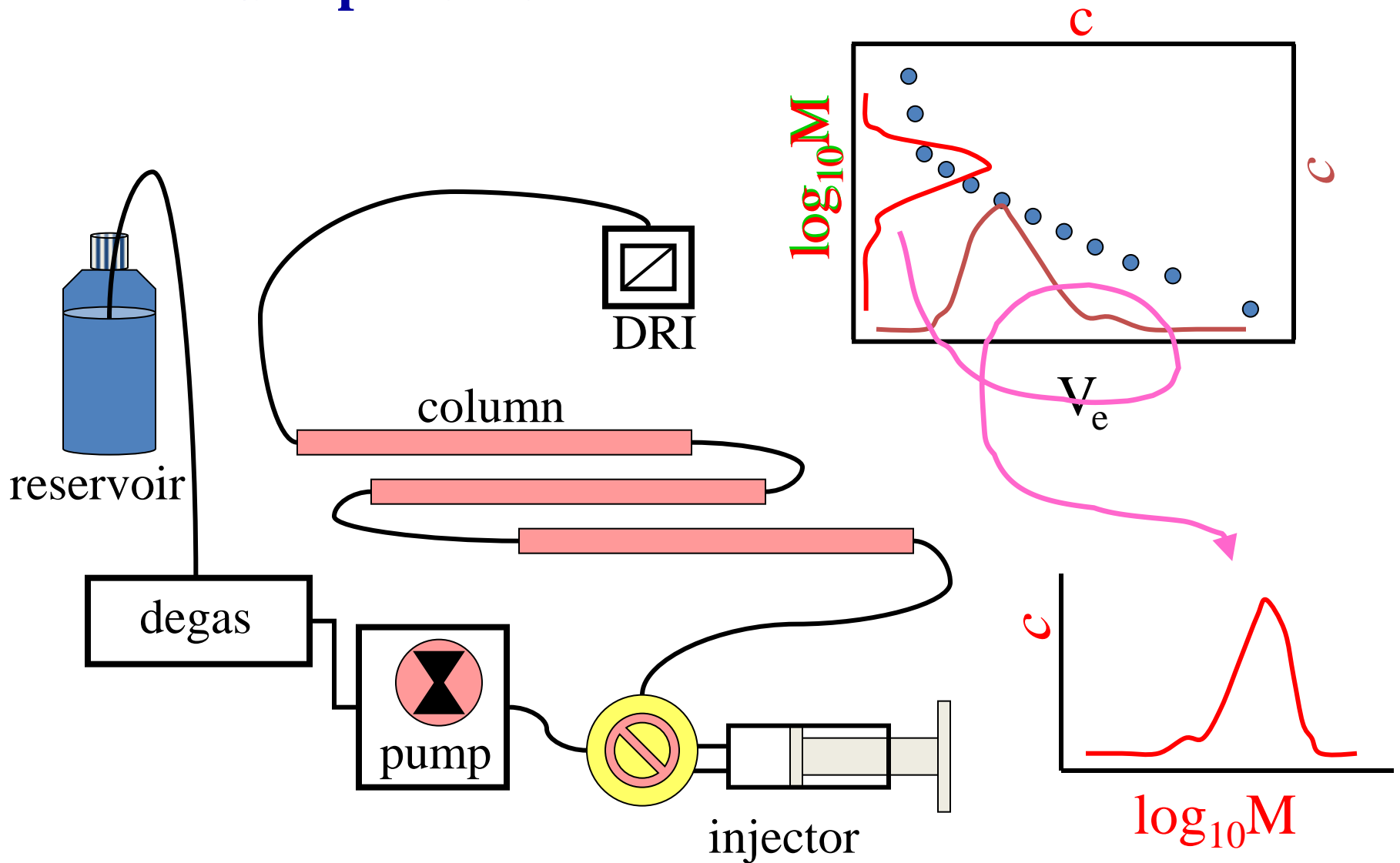
# Molecular Weight Distribution

## Gel Permeation Chromatography (GPC)

- **GPC or SEC (size exclusion chromatography)**
  - a. GPC method is modified column chromatography.
  - b. Packing material: Poly(styrene-co-divinylbenzene), glass or silica bead swollen and porous surface.
  - c. Detector : RI, UV, IR detector, light scattering detector
  - d. Pumping and fraction collector system for elution.
  - e. By using standard (monodisperse polystyrene), we can obtain  $M_n$ ,  $M_w$ .



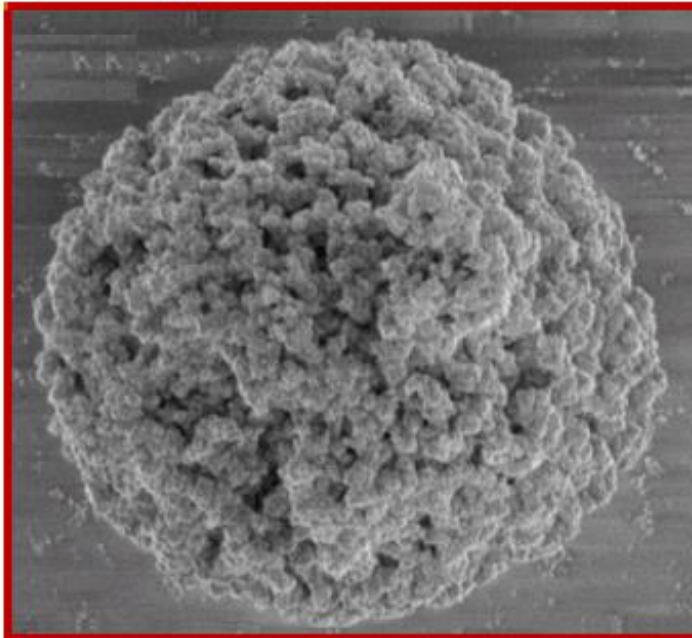
# Simple GPC



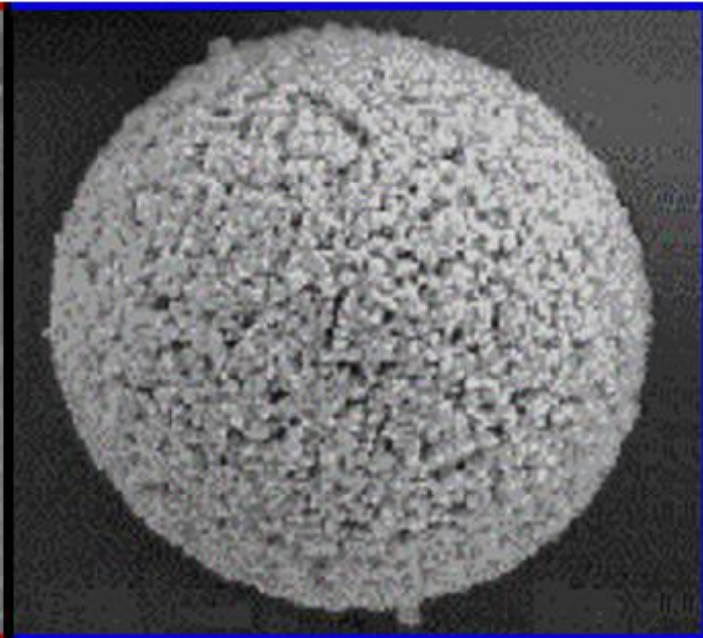
## GPC Column Packings

- GPC columns are packing with cross-linked, insoluble beads, typically co-polymers of styrene and divinyl benzene for organic GPC
- These beads have a rigid pore structure that remains intact in the presence of solvent

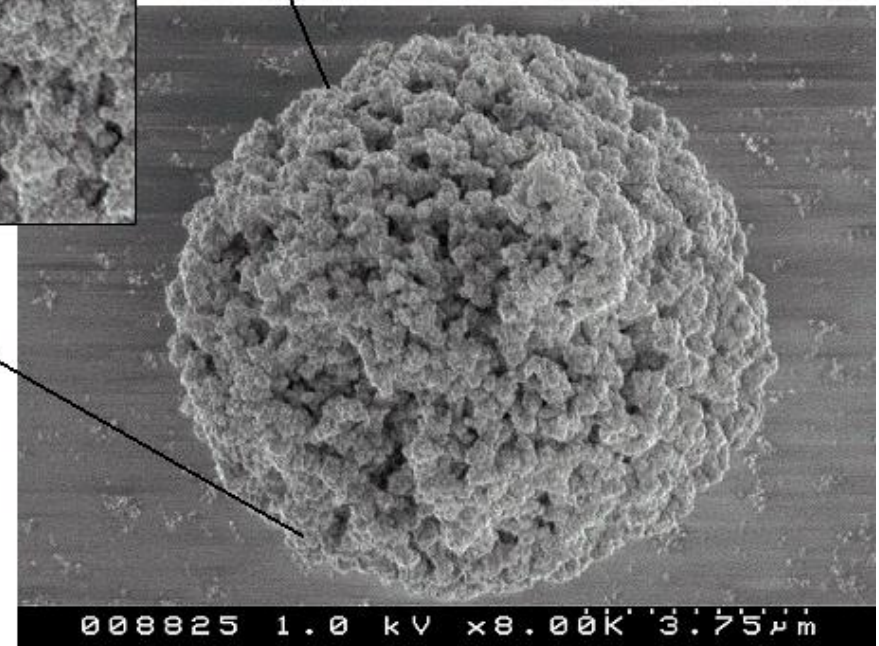
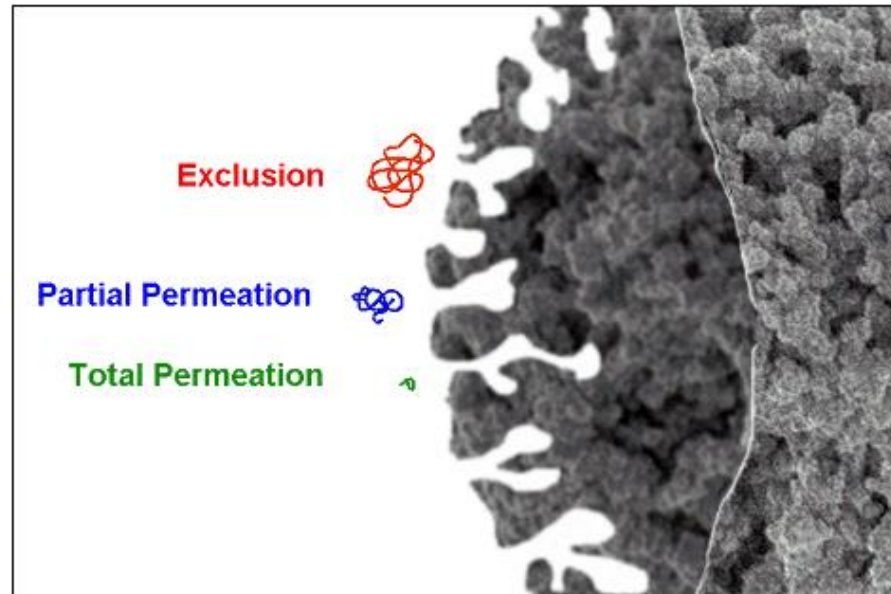
PLgel 10  $\mu\text{m}$   $10^6\text{A}$



PLgel 10  $\mu\text{m}$   $10^3\text{A}$



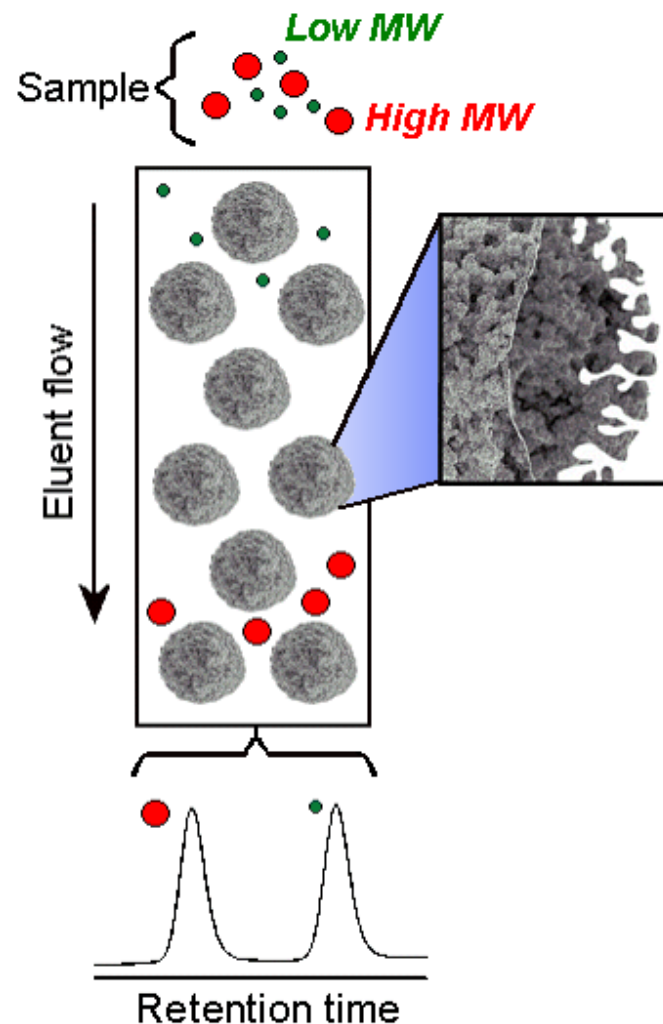
# Permeation of Polymer Molecules



- Polymer coils in solution can permeate the pores on GPC packing materials
- Exclusion, partial permeation and total permeation are possible

## GPC Separation Mechanism

- Polymer is prepared as a dilute solution in the eluent and injected into the system
- The GPC column is packed with porous beads of controlled porosity and particle size
- Large molecules are not able to permeate all of the pores and have a shorter residence time in the column
- Small molecules permeate deep into the porous matrix and have a long residence time in the column
- Polymer molecules are separated according to molecular size, eluting largest first, smallest last

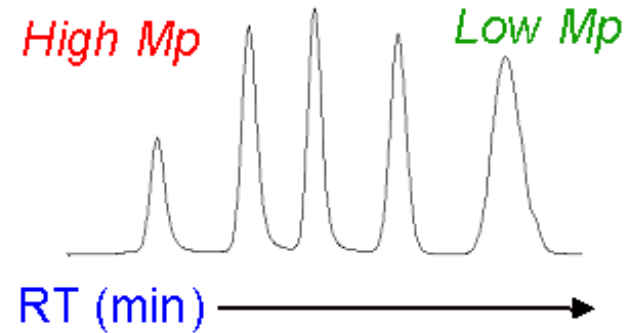




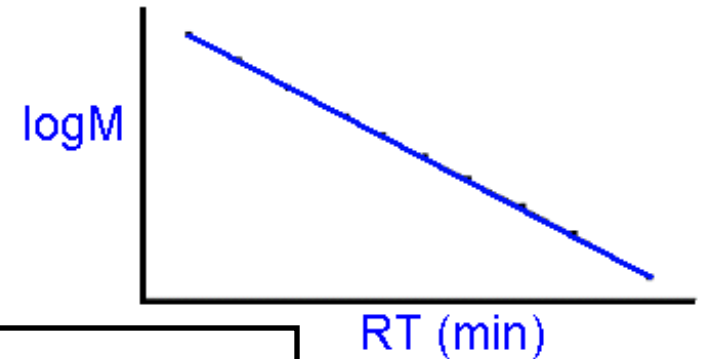
# Calibration of GPC Column Using Narrow Standards

- Chromatograph a series of well characterised, narrow polydispersity polymer standards
- Plot peak retention time (RT) versus peak log molecular weight (logM)
- Fit the data using a mathematical function
- The calibration curve will be characteristic of the GPC column set used

Chromatogram of narrow standards



GPC Calibration Curve



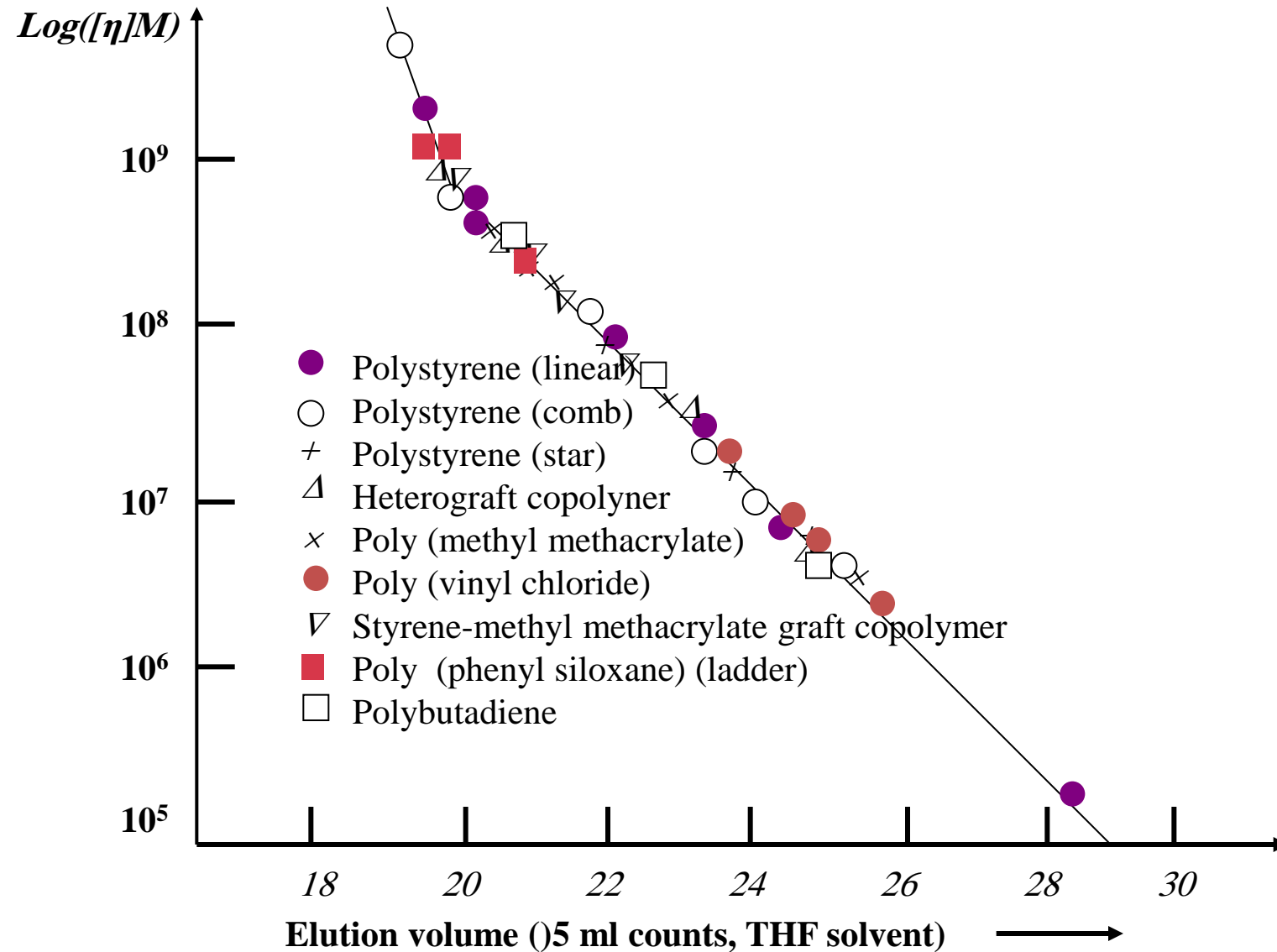
## Most commonly used polymer calibrants

**Polystyrene** - THF, toluene, chloroform

**Polymethyl methacrylate** - MEK, ethyl acetate, acetone, DMF

**Polyethylene oxide/glycol** - aqueous eluents, DMF, DMSO

# Universal calibration for gel permeation chromatography. THF, tetrahydrofuran.



## B. Universal calibration method

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$$[\eta]_1 M_1 = [\eta]_2 M_2$$

to be combined Mark-Houwink-Sakurada equation

$$\log M_2 = \left( \frac{1}{1 + a_2} \right) \log \left( \frac{K_1}{K_2} \right) + \left( \frac{1 + a_1}{1 + a_2} \right) \log M_1$$