

Chapter 6. Characterization of Molecular weight

- All the polymers have molecular weight distribution (MWD)
- \bar{M}_n number-average molecular weight ()

$$\bar{M}_n = \frac{W}{N} = \frac{\sum_{x=1}^{\infty} n_x M_x}{\sum_{x=1}^{\infty} n_x} = \frac{n_1 M_1}{\sum_{x=1}^{\infty} n_x} + \frac{n_2 M_2}{\sum_{x=1}^{\infty} n_x} + \dots$$

$$= \sum_{x=1}^{\infty} \left(\frac{n_x}{N} \right) M_x = \frac{\sum_{x=1}^{\infty} n_x M_x}{\sum_{x=1}^{\infty} n_x}$$

Where W = total sample weight

N = total number of moles in the sample

n_x = number of moles of x-mer

M_x = molecular weight of x-mer

- \bar{M}_w = weight average molecular weight ()

$$\bar{M}_w = \frac{\sum_{x=1}^{\infty} W_x M_x}{\sum_{x=1}^{\infty} W_x} = \frac{W_1 M_1}{\sum_{x=1}^{\infty} W_x} + \frac{W_2 M_2}{\sum_{x=1}^{\infty} W_x} + \dots$$

$$= \sum_{x=1}^{\infty} \left(\frac{W_x}{W} \right) M_x = \frac{\sum_{x=1}^{\infty} n_x M_x^2}{\sum_{x=1}^{\infty} n_x M_x}$$

where W_x = weight of x-mer in sample = $n_x M_x$

ex) calculate \bar{M}_n and \bar{M}_w for a sample of PP with the following composition

$M_i = 10000$	$n_i = 5$
15000	7
20000	8
23000	13

30000	19
40000	10
50000	5

$$\frac{\sum n_i M_i}{\sum n_i} = \frac{5(10,000) + 7(15,000) + 8(20,000) + 13(23,000) + 19(30,000) + 10(40,000) + 5(50,000)}{5 + 7 + 8 + 13 + 19 + 10 + 5}$$

$$= \frac{1,834,000}{67}$$

$$\frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{5(10,000)^2 + 7(15,000)^2 + \dots + 5(50,000)^2}{1,834,000}$$

$$= \frac{5.7752 * 10^{10}}{1,834,000}$$

$$\frac{\overline{M}_w}{\overline{M}_n} = \frac{31,490}{27,373}$$

Degree of Polymerization

$$x = \frac{M_n}{M} = \frac{27,373}{42} \cong 652$$

propylene M=42g/mol

M_z ► z-average molecular weight

$$M_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2}$$

$$M_z > M_w > M_n$$

$$M_z = M_w = M_n \quad \text{when MWD} = 1.0 \text{ or monodisperse}$$

Molecular weight of Mixtures (Blends)

$$(M_n)_{blend} = \left[\frac{w_1}{(M_n)_1} + \frac{w_2}{(M_n)_2} \right]^{-1}$$

where w_1 = weight fraction of polymer 1

$$(M_w)_{blend} = \sum w_i (M_w)_i = w_1 (M_w)_1 + w_2 (M_w)_2$$

EX) A Polymer $M_n=50,000$ $M_w=250,000$

$$w_A=0.7 \quad , \quad MWD = 5.0$$

B Polymer $M_n=100,000$ $M_w=300,000$

$$w_B=0.3 \quad , \quad MWD = 3.0$$

$$(M_n)_{blend} = \left[\frac{0.7}{50,000} + \frac{0.3}{100,000} \right]^{-1} = 58,800$$

$$(M_w)_{blend} = 0.7(250,000) + 0.3(300,000) = 265,000$$

$$(MWD)_{blend} = \frac{265,000}{58,800} = 4.50$$

Chapter 6. The Molecular Weight of Polymers

Broad molecular weight distribution(MWD)



Fig. GPC Chromatogram

Table 6.1 Hypothetical distribution of balls

Number of balls, N_i	Diameter D_i (inch)	Length $N_i D_i$	Area $N_i D_i^2$	Volume $N_i D_i^3$
900	1	900	900	900
50	5	250	1250	6250
50	25	1250	31250	781250
$\sum N_i = 1000$		$\sum N_i D_i = 2400$	$\sum = 33400$	$\sum = 788400$

(1) Average diameter (D_L , based on length) (one dimension)

$$D_L = \frac{\sum N_i D_i}{\sum N_i} = \frac{2400}{1000} = 2.4(\text{inch})$$

- Table 6.1 , 1 inch ball percent Total volume 0.1%

(2) Average diameter (D_A , based on area) (two dimension)

$$D_A = \frac{\sum N_i D_i^2}{\sum N_i D_i} = \frac{33400}{2400} = 13.9(\text{inch})$$

(3) Average diameter (D_V , based on volume) (three dimension)

$$D_V = \frac{\sum N_i D_i^3}{\sum N_i D_i^2} = \frac{788400}{33400} = 23.6(\text{inch})$$

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$$M_n = \frac{\text{total weight of system}}{\text{molecules in system}} \quad (6.1)$$

- (1) (M_n) : number -average molecular weight
- (2) (M_w) : weight -average molecular weight
- (3) z (M_z) : Z-average molecular weight
- (4) (M_v) : viscosity -average molecular weight

$$M_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{\sum w_i}{\sum (w_i / M_i)} \quad (\text{since } w_i = N_i M_i)$$

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum w_i M_i}{\sum w_i}$$

$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum N_i w_i^2}{\sum N_i w_i}$$

$$[\eta] = K[M]^\alpha \quad (K \quad \alpha \quad \text{Mark-Houwink})$$

N_i = the number of each species

M_i = molecular weight of each polymer species

η = Intrinsic viscosity ()

$$\text{sol) } M_w = \frac{\sum w_i M_i}{\sum w_i} = \sum w_i (M_w)_i$$

$$w_i = \frac{w_i}{\sum w_i} \quad (\text{weight fraction} = w_i)$$

$$250,000 = 500,000 w_A + 250,000 w_B + 125,000(1 - w_A - w_B)$$

$$w_A = 0.333 - 0.333 w_B \quad \text{-(A)}$$

$$M_n = \frac{\sum w_i}{\sum (w_i / M_i)}$$

$$\frac{1}{M_n} = \sum \frac{w_i}{(M_n)_i} \quad , \quad \text{MWD} = \frac{M_w}{M_n}$$

$$\frac{1}{250000 / 3.65} = \frac{w_A}{500000 / 2.50} + \frac{w_B}{250000 / 2.00} + \frac{1 - w_A - w_B}{125000 / 2.50}$$

$$w_A = 0.360 - 0.800 w_B \quad \text{-(B)}$$

(A) (B)

$$w_A = 0.058 \quad , \quad w_B = 0.314 \quad , \quad w_C = 0.628$$

$$A = 2900 \text{ kg} \quad B = 15700 \text{ kg} \quad C = 31400 \text{ kg}$$

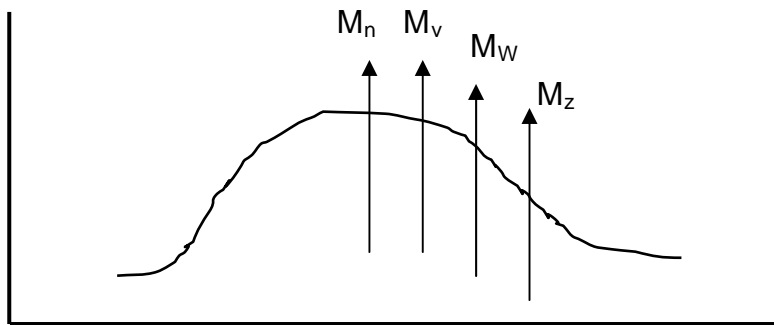


Fig. GPC chromatogram :

$$M_z \geq M_w \geq M_v \geq M_n$$

when $\text{MWD} = 1.0$, $M_z = M_w = M_v = M_n$

$$= \frac{M_w}{M_n}$$

Ex 6.1) Polyethylene A, B, C 가 . blending M_w 가 250000
 MWD 가 3.65 DLS 50000kg . PE , A, B,C ?

Lot.	M_w	MWD(PDI)
A	500000	2.50
B	250000	2.00
C	125000	2.50

Gel Permeation Chromatography(GPC)

Size Exclusion Chromatography(SEC)

- polymer molecules are separated according to their sizes.

-GPC

(1) Column

(i) organic solvent column

(ex) μ -styragel

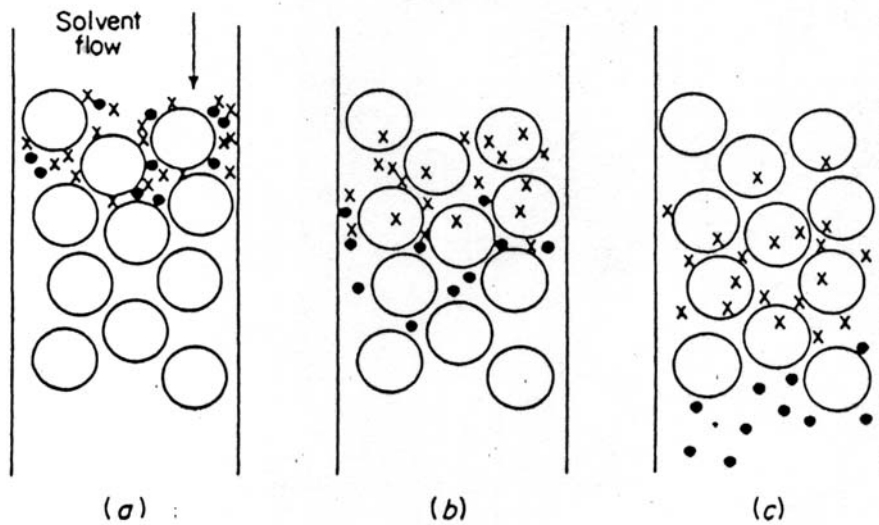
- packing material styrene-divinyl benzene crosslinked copolymer

- pore size 100\AA , 500\AA , 10^3 , 10^4 , 10^5 , 10^6\AA

(ii) Aqueous solvent column

(ex) Waters I-125

- protein biopolymer



x Small molecules

• Large molecules

Figure 6.8 Process of gel permeation (size exclusion) chromatography [9]: (a) elution; (c) continued elution

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Molecular weight measurements

(1) M_n

(a) Membrane osmometry ($M_n \geq 30,000$)

(b) Vapor phase osmometry ($M_n < 30,000$)

(c) End - group

(2) M_w

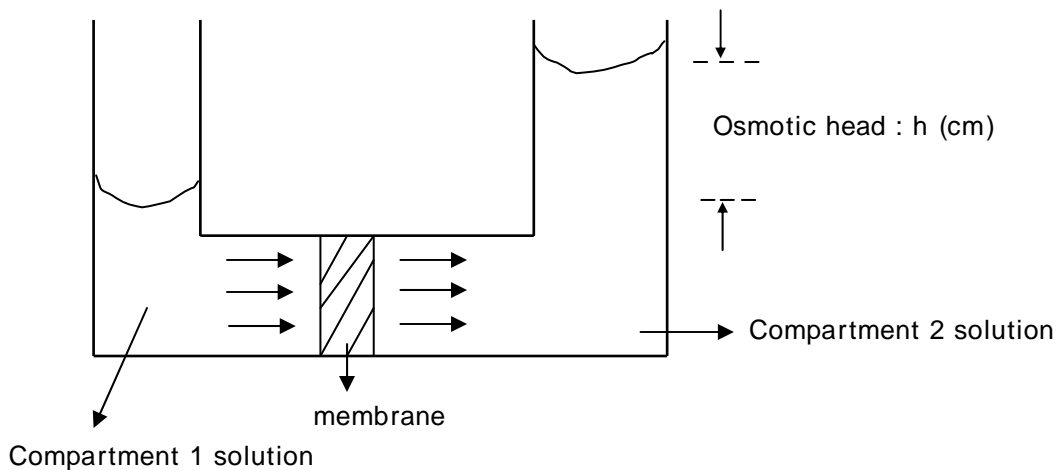
(a) Light scattering

(3) GPC $M_n, M_w, M_z, MWD = M_w/M_n$

(4) Viscosity () - M_v (Ubbelohde)

$[\eta] = K[M]^\alpha$, (K α Mark -Houwink)

(a) Membrane osmometry



Ex) Determine M_n when $h=10\text{cm}$, in toluene at 25°C , conc. = $0.02 \text{ (g/cm}^3\text{)}$

Osmotic pressure $\Pi = \rho gh$ $\rho = \text{(g/cm}^3\text{)}$, $g = 980 \text{ (cm/sec}^2\text{)}$

$$M_n = \frac{RT}{\frac{\pi}{C}} = \frac{(8.314 \times 10^7 \text{ erg})(273 + 25)K(0.02 \text{ g/cm}^3)}{(\text{mol} \cdot K)(0.866 \text{ g/cm}^3)(980 \text{ cm/sec}^2)(10 \text{ cm})} = 58390 \text{ (g/mol)}$$

The Osmotic pressure of an Ideal solution

$$\frac{\pi}{c} = \frac{RT}{M} + \frac{RTV_1^0}{2M^2}C_2 + \frac{RT(V_1^0)^2}{3M^3}C_2^2 + \dots$$

The osmotic data of a real solution :

$$\frac{\pi}{c} = \frac{RT}{M_n} + RT(A_2C + A_3C^2 + \dots).$$

where A_2 and A_3 are the 2nd and 3rd virial coefficient

Factors affecting the A_2

- i) the nature of polymer and solvent
- ii) MWD and M_w and M_n
- iii) Conc and temp. of solution
- iv) Branching in the polymer chain

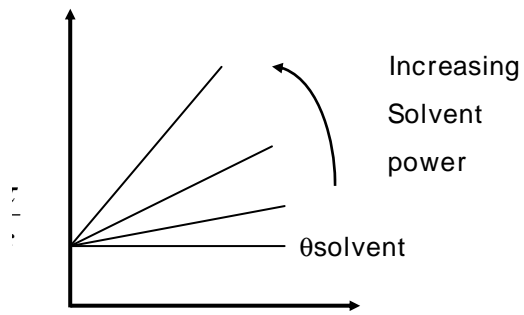
- better solvent results higher A_2
- M_w M_n branching 가 $A_2 \downarrow$
- Temp 가 $A_2 \uparrow$
- Temp 가 $A_2 \downarrow$

θ (theta) temperature

-temperature at which a given polymer species of infinite molecular weight be insoluble at great dilution in a particular solvent ($A_2=0$)

(the diameter of the polymer chain in solution = the diameter in the amorphous bulk polymer)

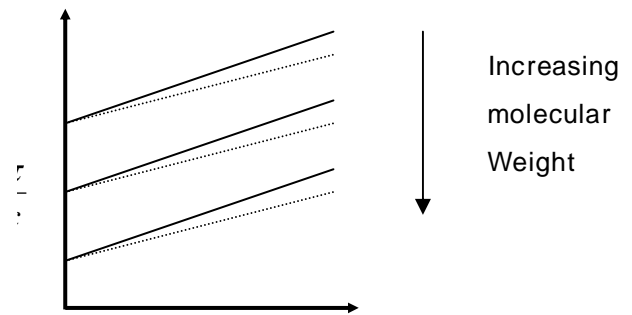
unperturbed state = the solvent neither expands nor contracts the macromolecules



C

(a)

Same polymer sample
in different solvents.



C

(b)

Different molecular weight,
sample polymer type, in a
same solvent

- second virial coefficient

$$\frac{\pi}{c} = \frac{RT}{M_n} + \frac{RT}{1} (A_2 C) = RT \left(\frac{1}{M_n} + A_2 C \right)$$

$$A_2 = \left(\frac{1}{2} - \chi \right) / (L V_1^0 V_2^2)$$

V_2 : specific volume of the polymer

L: Avogadro's No

V_1^0 : molar volume of the solvent

χ : interaction energy per mole/RT

“Flory -Huggins interaction parameter”

- Better solvents have lower χ value, higher A_2 .

- when $\chi_{12} = 0.5$, $A_2 = 0$ (θ solvent)

b) Viscosity Average Molecular Weight, \bar{M}_v

- The viscosity of dilute polymer solution is higher than that of the pure solvent.
- Viscosity depends on (temperature, nature of solvent and polymer, polymer \bar{M}_v , size of polymer)

- Mark -Houwink -Sakurada Equation:

$$[\eta] = K \bar{M}_v^\alpha$$

where K AND α are constants, depend on polymer type, solvent and solution temperature.

Ex) Determine \bar{M}_v for polystyrene at 25 °C in Toluene.

(given data): $\alpha=0.69$, $K=17 \cdot 10^{-5}$

$$[\eta]=0.6(\text{dl/g})$$

$$0.6(\text{dl/g}) = 17 \cdot 10^{-5} (\text{dl/g})^{-1} \cdot \bar{M}_v^{0.69}$$

$$\therefore \bar{M}_v = 138,500$$

- Measurement of Intrinsic Viscosity

$$\eta_r = \frac{\eta}{\eta_s} = 1 + 2.5\phi \quad (\text{by Einstein})$$

(for suspension of rigid, noninteracting spheres)

where η_r : relative viscosity

η : viscosity of suspension

η_s : viscosity of the solvent

ϕ : volume fraction of spheres

$$\left(\frac{\eta}{\eta_s} - 1 \right) = \eta_{sp} = 2.5\phi$$

η_{sp} = specific viscosity

$$\left(\frac{\eta}{\eta_s} - 1\right) = \eta_{sp} = KC$$

where K is a function of the size of polymer, shape, rigidity, the interactions between molecules, etc.

Ultimately, K depends on the particular polymer-solvent system, temperature, the size of the molecules in solution.

$$\left(\frac{\eta}{\eta_s} - 1\right)^{-1}/c = r_{red} = K$$

r_{red} : reduced viscosity

when $c \rightarrow 0$, then (dilute solution)

$$\lim_{c \rightarrow 0} \left(\frac{\eta_{sp}}{c}\right) = [\eta]$$

$[\eta]$: intrinsic viscosity

* The intrinsic viscosity is a function of the size of the polymer molecules in solution, polymer-solvent system, and the temperature.

* If measurements are made in constant temp and specified solvent, then should be related to the polymer's molecular weight.

(Ex) Determine $[\eta]$ and \bar{M}_v for polystyrene in toluene at 25 °C,

(Ubbelohde viscometer)

$$K = 4.2 \cdot 10^{-3} \text{ (dl/g)}, \alpha = 0.69, t_0 = 90 \text{ sec}$$

(Sol)

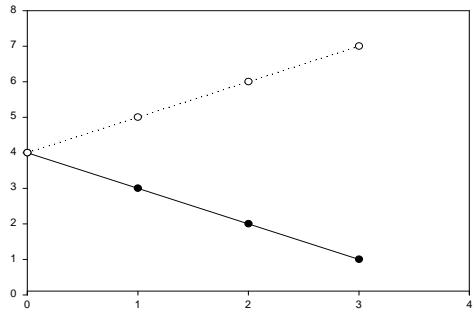
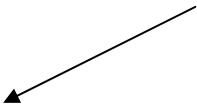
t	Conc(g/dl)
105	0.275
120	0.444
155	0.896
180	1.110

$$\frac{\eta}{\eta_0} \cong \frac{t}{t_0} \quad (\eta \text{ solution viscosity})$$

η_0 solvent viscosity)

Huggins Eq

$$\frac{1}{c} \left(\frac{\eta}{\eta_0} - 1 \right) = [\eta] + K_H [\eta]^2 c$$



Kraemer Eq

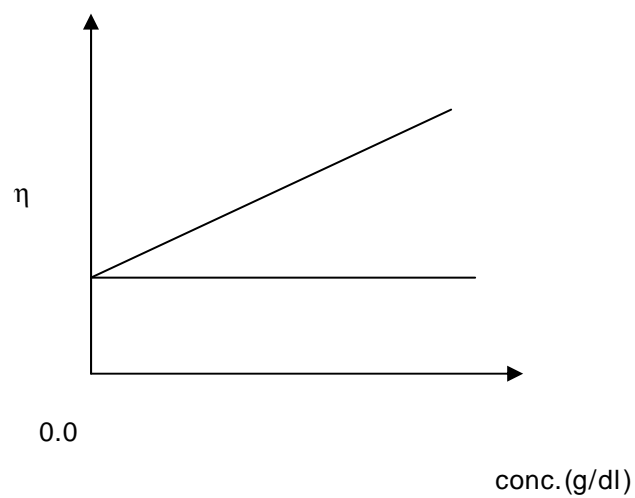
$$\frac{1}{c} \ln \left(\frac{\eta}{\eta_0} \right) = [\eta] + K_1 [\eta]^2 c$$



K_H : huggins
 K_1 : Kreamer

$\frac{\eta}{\eta_0} \cong \frac{t}{t_0}$	$\frac{\eta}{\eta_0} - 1$	$\frac{1}{c} \left(\frac{\eta}{\eta_0} - 1 \right)$	$\frac{1}{c} \ln \left(\frac{\eta}{\eta_0} \right)$
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1.167	0.167	0.607	0.562
1.333	0.333	0.750	0.647
1.722	0.722	0.806	0.607
2.000	1.000	0.900	0.624



Also we can get K_H and K_1 from $[\eta]$ value.

(c) Gel Permeation Chromatography (GPC)

-Polymer molecules are separated according to their sizes.

:

(1) column

ex) Water Associates. Column for organic solvents :

Packing material: styrene -divinyl benzene copolymer.

Pore size: 100 \AA , 500 \AA , 10^3 , 10^4 , 10^5 , 10^6 \AA

(2) Detectors

a) differential refractometer

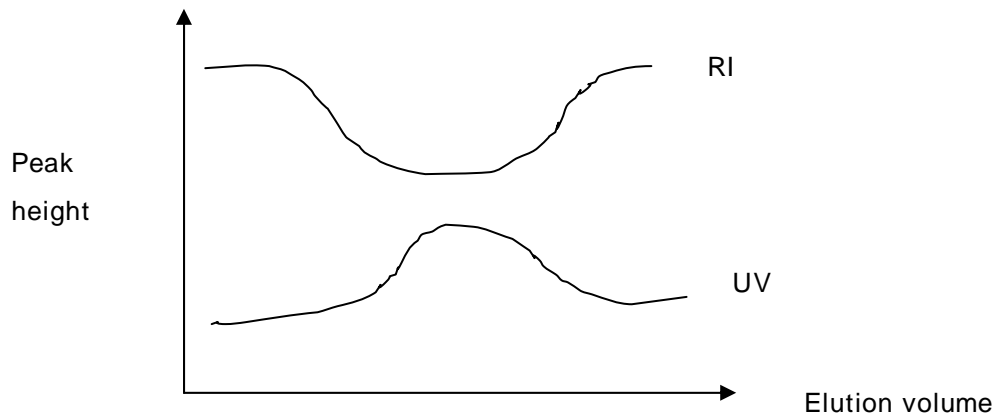
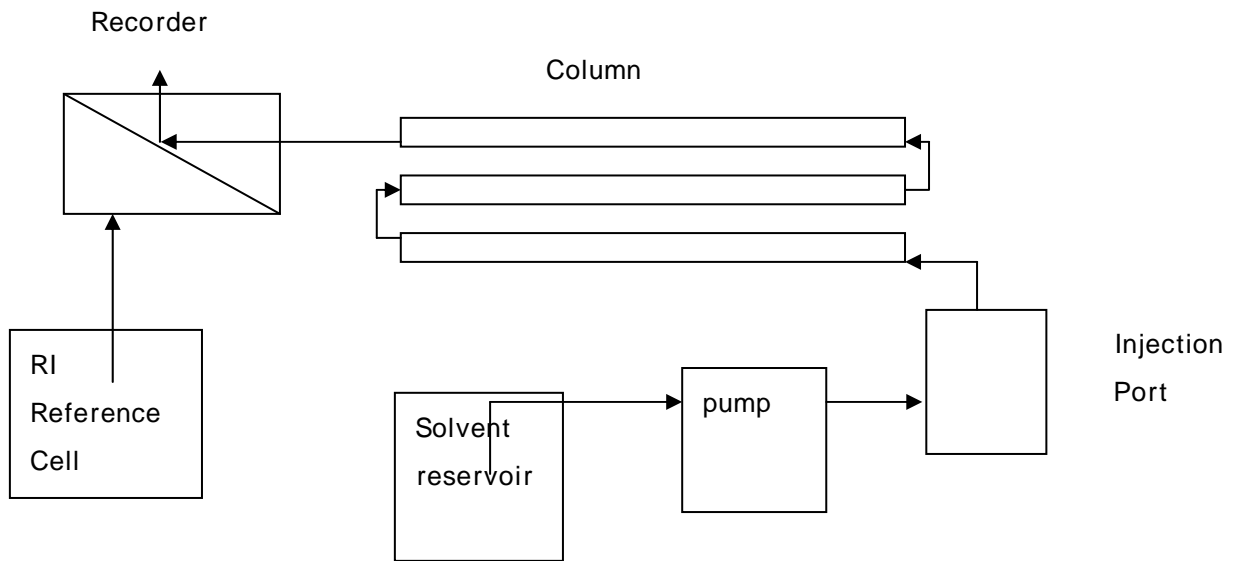
b) UV detector

(3) Pump (Solvent Delivery System)

-pressure range : 0~6000psi

(4) Injection of Sample

(5) Recorder or Microcomputer



GPC Chromatogram

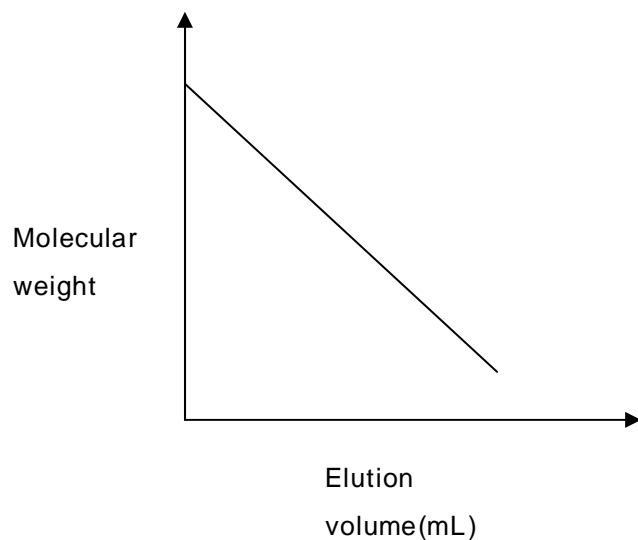
Ex) PE, PC

-GPC Calibration

(1) Direct Calibration - PS standards, narrow MWD

(2) Indirect Calibration – Universal Calibration Method

(1) Direct Calibration : using PS standards with known Molecular weight



(2) Universal Calibration : (Hydrodynamic Volume Concept):

$$[\eta]_i M_i = K_i (M_i)^{\alpha_i+1} \quad (\text{Mark -Houwink Eq})$$

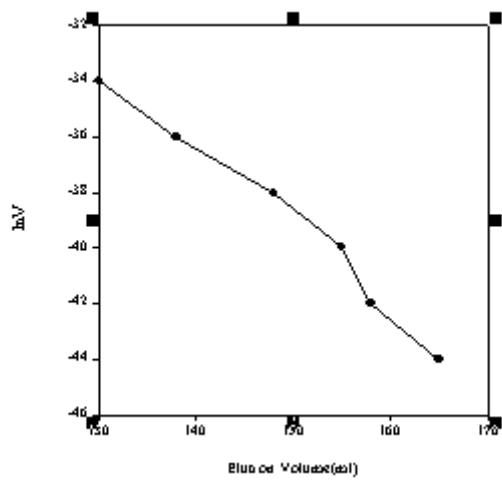
at equal elution volumes;

$$[\eta]_1 M_1 = K_1 (M_1)^{\alpha_1+1} = [\eta]_2 M_2 = K_2 M_2^{\alpha_2+1}$$

$$V = \frac{4\pi[\eta]M}{9.3 \cdot 10^{24} + 4\pi Lc([\eta] - [\eta]_{\theta})} \quad \text{Rudin's(3-17)}$$

L: Avogadro's number

$$\text{At } c \rightarrow 0, V = 4\pi [\eta] M / (9.3 \cdot 10^{24})$$



, PS hydrodynamic volume, K, α
 , sample K, α
 hydrodynamic volume in same solvent, temp

(Ref) A.Ruin, "The Elements of Polymer Science and Eng."
 Academic Press(1982),chap 3, p115