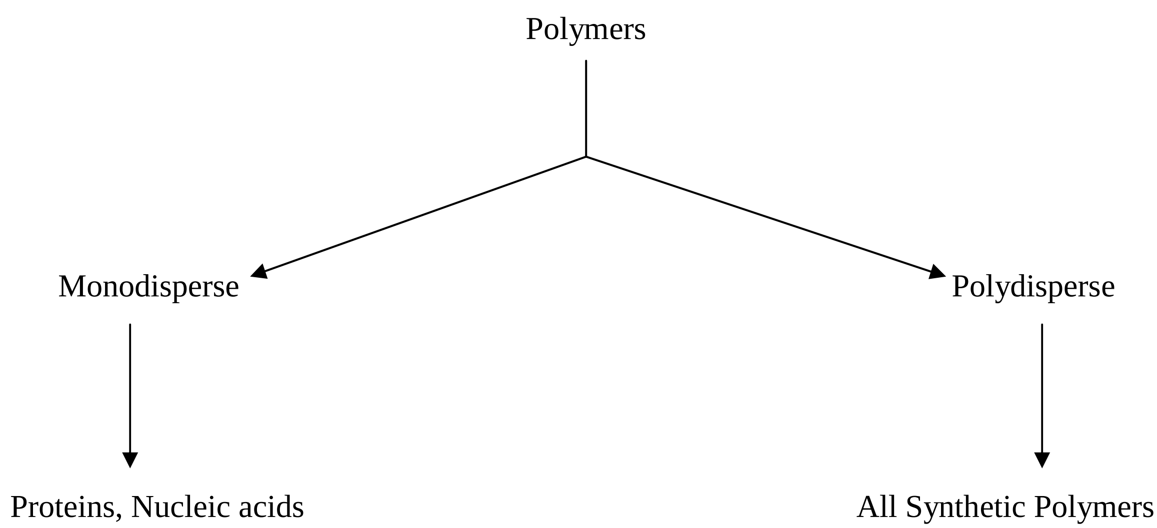
Molecular Weight Analysis of Polymers

Properties dependent on Molecular Weights and Molecular Weight Distributions (MWD)

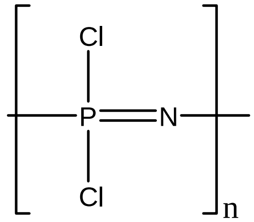
- Melt Viscosity
- Tensile Strength
- Toughness or Impact Strength
- Resistance to heat
- Corrosive Properties



Average Molecular Weight ($\overline{M}$)

$\overline{M}$ **= Average Number of Repeating Units** $\overline{n}$ **or** $\overline{dp}$

Examples:

(1) Find $\overline{M}$ for  $_n$ if n = 10,000?

2 X Cl = 70.9
1 X P = 31.0
1 X N = 14.0

Molecular Weight of repeating Unit = 115.9 ~116

$\overline{M}$ **= n or dp x** Mol. Weight of repeating units

= 10,000 X 116 = 11,600,00

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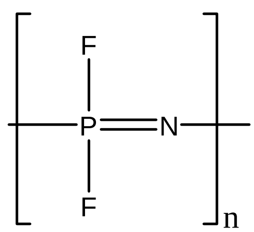
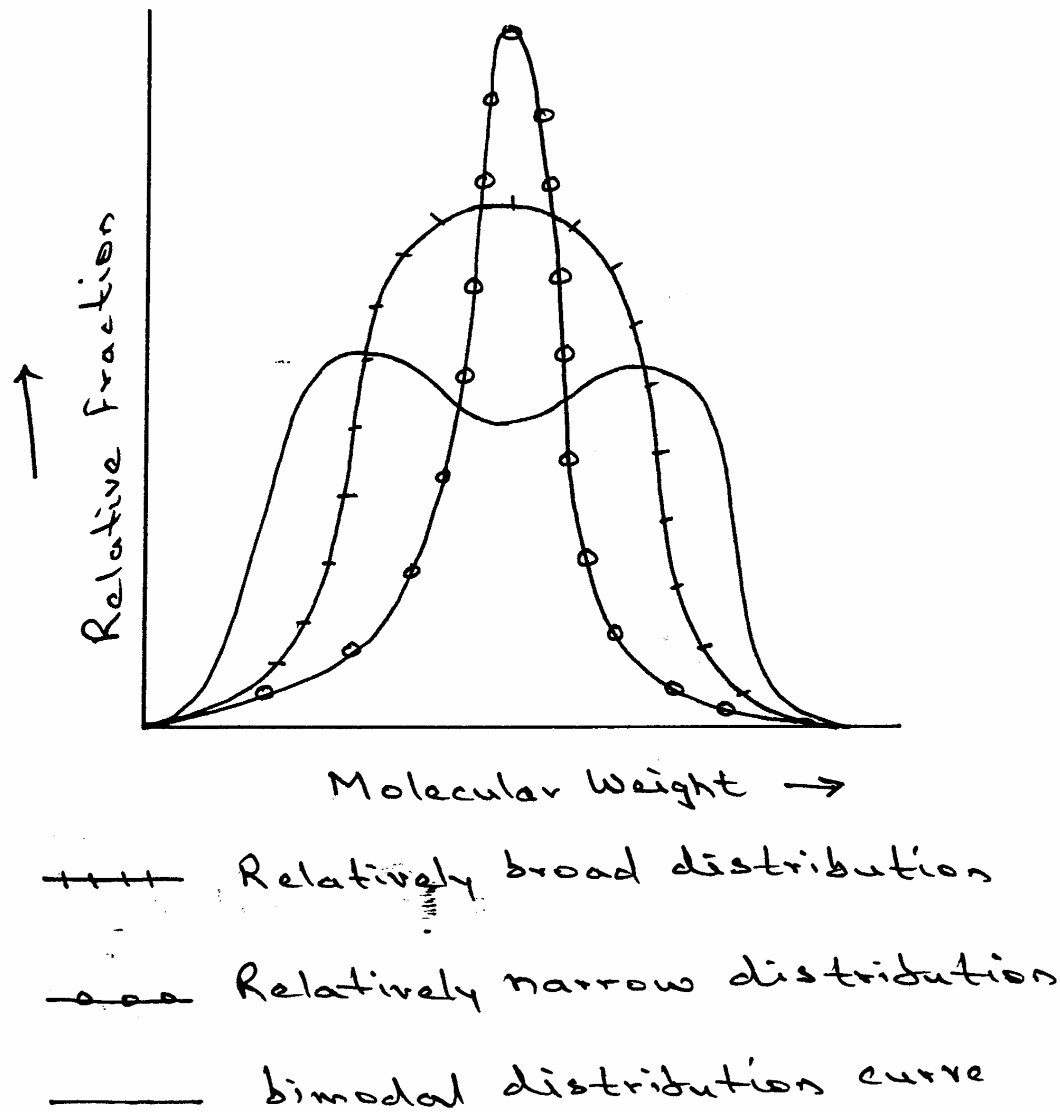
(2) Find $\overline{M}$ for  $_n$ n = 5,000?

Answer: 415,000

Representative Differential Weight Distribution Curve



- Bimodal distribution is characteristic of polymerization occurring under two different pathways or environments.

Number Average Molecular Weight

Mathematically, in a mixture of polymer molecules with different molecular weights in which the number of molecules having a particular molecular weight, M_i, is given by N_i. The "number-average" probability (P_i) of a given mass being present is

$$P_i = \frac{N_i}{\sum_{j=0}^{\infty} N_j}$$

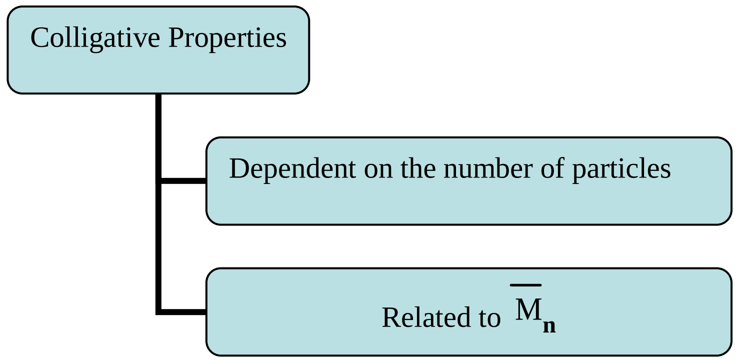
Indeed, the number-average molecular weight is given by the formula

$$\overline{M_n} = \sum_{i=0}^{\infty} \left(\frac{N_i}{\sum_{j=0}^{\infty} N_j} \right) M_i = \frac{\sum_{i=0}^{\infty} N_i M_i}{\sum_{j=0}^{\infty} N_j}$$

$\overline{M}_{\mathbf{n}}$ is the arithmetic mean, representing the total weight of the molecules present divided by the total number of molecules. It is important to recognize that most thermodynamic measurements are based on the number of molecules present and hence depend on the number-average molecular weight: examples are the colligative properties, osmotic pressure and freezing point depression. End-group analysis is also used to calculate a value for $\overline{M}_{\mathbf{n}}$.

Number Average molecular weight $\overline{M}_{\mathbf{n}}$

Example : $\overline{M}_{\mathbf{n}}$ for molecules having molecular weights of 1.00×10^5, 2.00×10^5, 3.00×10^5 would be, $6.00 \times 10^5 / 3 = 2.00 \times 10^5$



$\overline{M}_n$ values are independent of molecular size

$\overline{M}_n$ values are highly sensitive to small molecules present in the mixture.

$\overline{M}_n$ values are determined by Rault's techniques that are dependent on "Colligative Properties"

(a) Ebulliometry (Boiling Point Elevation)

(b) Cryometry (Freezing point depression)

(c) Osmometry

Weight Average Molecular Weight

The probability factor in a weight-average considers the mass of the molecules so that the heavier molecules of the polymer segment are more important.

$$P_i = \frac{N_i M_i}{\sum_{j=0}^{\infty} N_j M_j}$$

The weight average formula is derived as follows:

$$\overline{M}_w = \sum_{i=0}^{\infty} \left(\frac{N_i M_i}{\sum_{j=0}^{\infty} N_j M_j} \right) M_i = \frac{\sum_{i=0}^{\infty} N_i M_i^2}{\sum_{j=0}^{\infty} N_j M_j}$$

Molecular weight measurements take into consideration the contributions of molecules according to their sizes give weight-average molecular weights. Light scattering and ultracentriguge methaods are routinely used in the determination of $\overline{M}_{\mathbf{w}}$**.**

It is important to recognize that the weight-average molecular weight is larger than or equal to the number-average molecular weight. Indeed, the ratio of the weight-average and number-average molecular weights, $\overline{M}_{\mathbf{w}}/\overline{M}_{\mathbf{n}}$, is a measure of the polydispersity of a polymer-mixture –this ratio is an index of how widely distributed the range of molecular weights are in the mixture.

Example:
For three molecules with molecular weights of 1.00 x 10^5, 2.00 x 10^5 and 3.00 x 10^5.

$\overline{M}_{\mathbf{w}}$ would be 2.33 x 10^5

Bulk properties of polymers such as viscosity and toughness are largely affected by $\overline{M}_{\mathbf{w}}$ values:

1. Light Scattering & 2. Ultracentrifugation techniques.

Average Molecular Weight ($\overline{M}_{\mathbf{z}}$)

$$\overline{M}_z = \frac{\sum_{i=1}^{\infty} M_i^3 N_i}{\sum_{i=1}^{\infty} M_i^2 N_i}$$

Example:

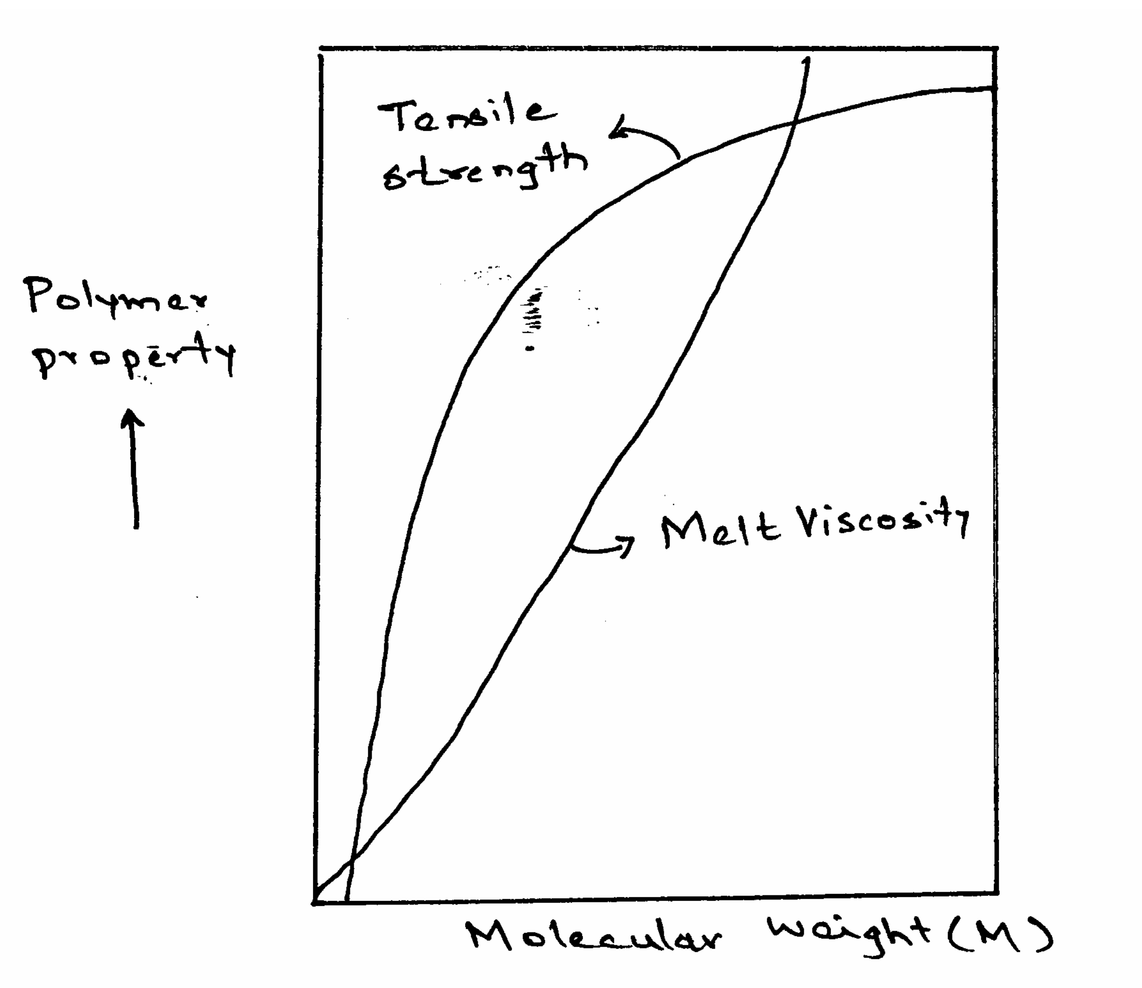
For three molecules with molecular weights of 1.00 x 10^5, 2.00 x 10^5 and 3.00 x 10^5.

$\overline{M}_z$ would be 2.57 x 10^5

Melt elasticity of polymers is largely dependent on $\overline{M}_z$ values. In a polydisperse system $\overline{M}_w > \overline{M}_n$, $\overline{M}_w = \overline{M}_n$ only in a monodisperse system.

Polydispersity Ratio or Index:

$\overline{M}_w / \overline{M}_n$ is a measure of polydispersity; it is 2.0 for condensation polymers.



For a polymer mixture which is heterogeneous with respect to molecular weight distributions, $\overline{M}_z > \overline{M}_z > \overline{M}_n$ with decrease in heterogeneity the various molecular weights will converge,

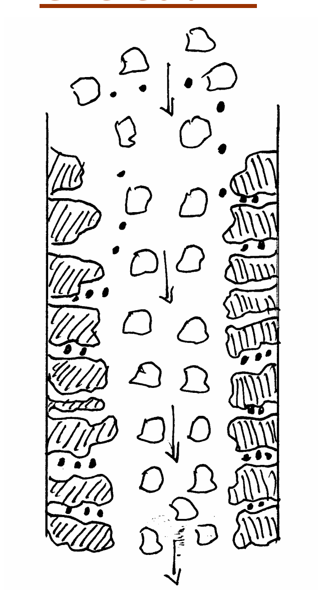
Finally, $\overline{M}_z = \overline{M}_z = \overline{M}_n$ → **Criterion for homogeneous polymer mixtures.**

Molecular Weight Determination of Polymers

1. Gel permeation Chromatography (GPC) Also called as Gel Filtration. This type of Liquid-Solid Elution Chromatography

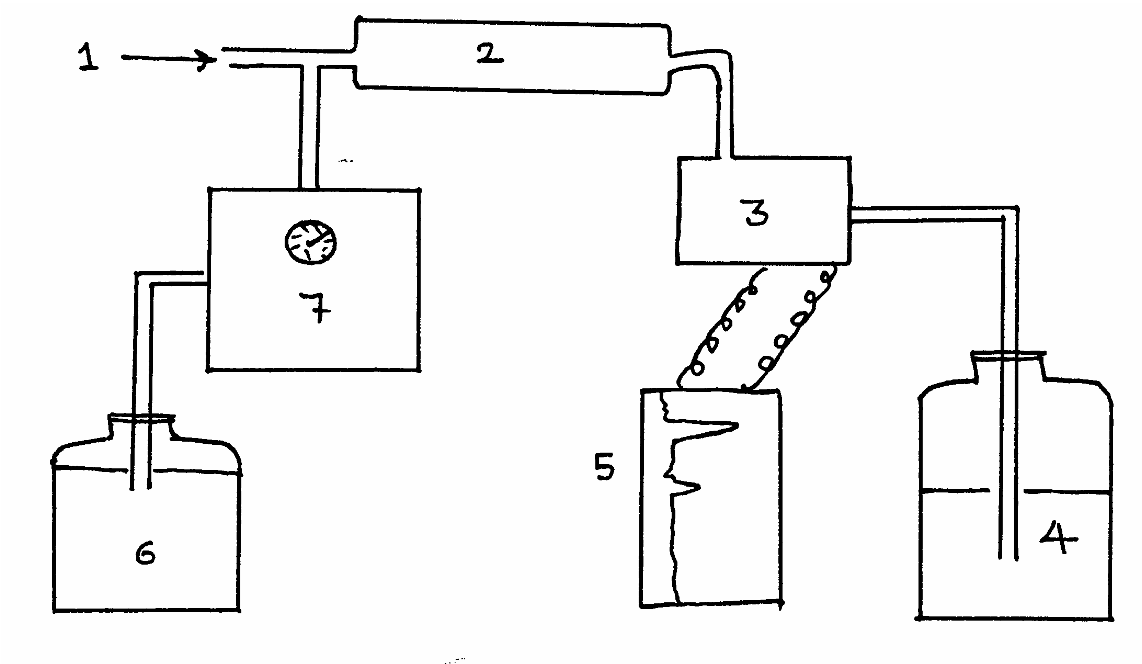
- Polymer fractions are separated on the basis of particle size
- Smaller particles permeate the gel preferentially
- The highest molecular weight fractions are eluted first
- Polystyrene gel with pore sizes 1 to 10^6 nm acts as a stationary phase.

GPC Column



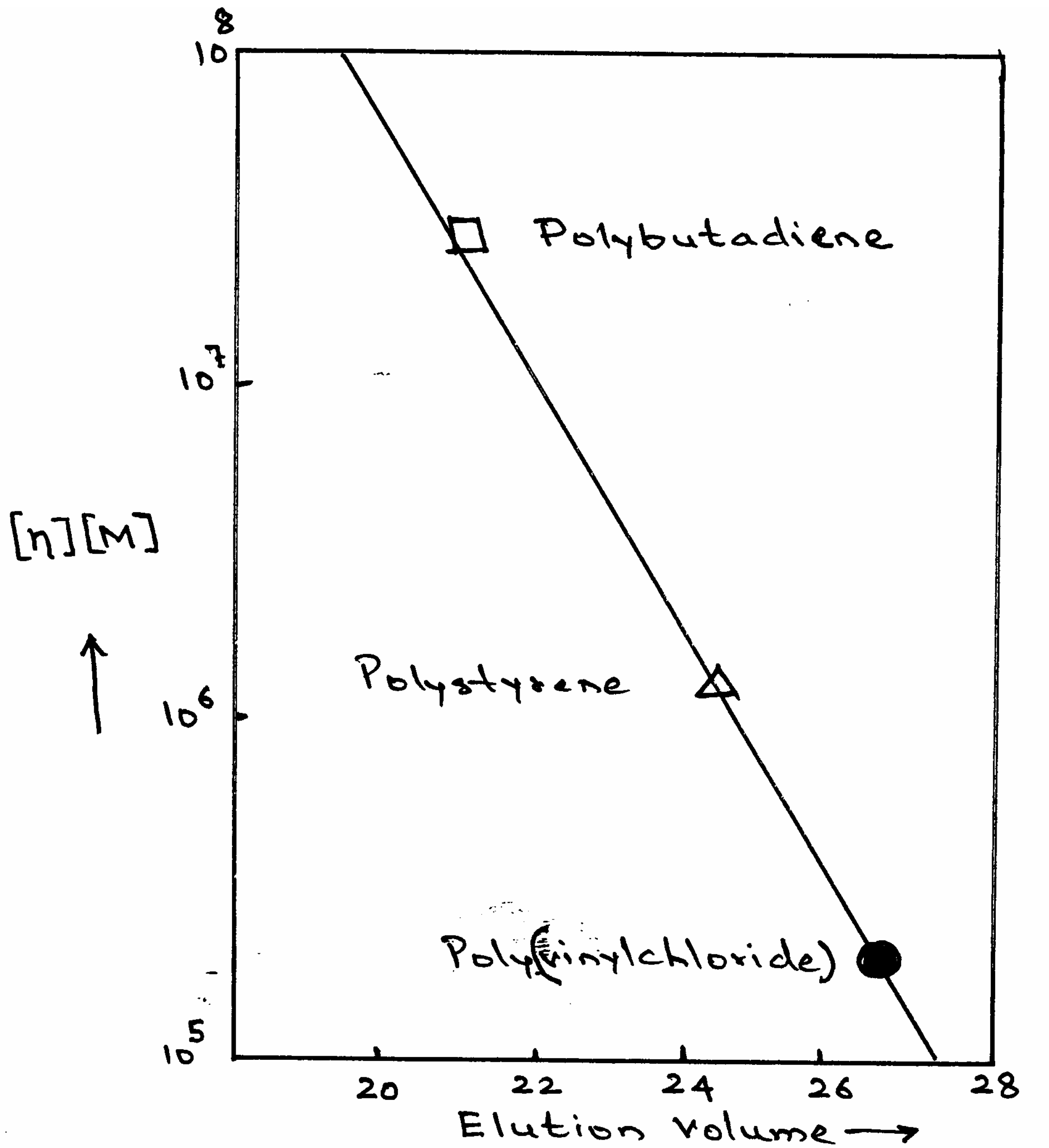
The mixture of different sized polymer molecules is eluted in a solvent through a column of porous particles. The smaller molecules can enter the pores, whereas the larger molecules move out.

Gel Permeation Chromatography Apparatus

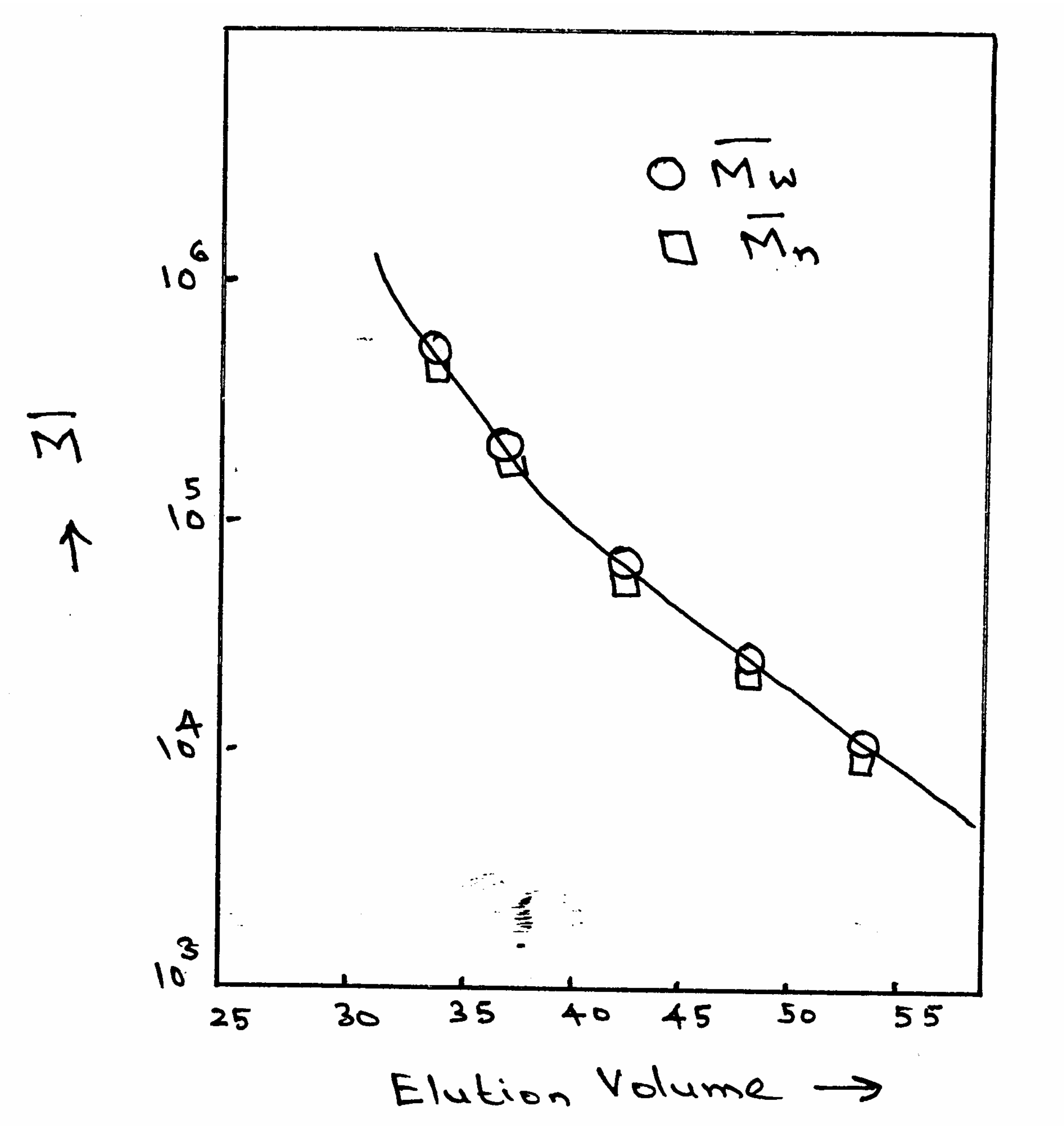


1. Injection Port
2. Column
3. Detector
4. Collector Flask
5. Chart Recorder
6. Solvent Reservoir
7. Pump with pressure gauge

Calibration Curve



Molecular Weight of Polystyrene standards in THF



Mathematically,

$\log[\eta]_X M_X = \log[\eta]_S M_s$ ------------------------------(1)

Where,

η = intrinsic viscosity, M = Molecular Weight, X= Unknown polymer and S = Standard Polymer

$$[\eta]_j = K_j M_j^{aj}\text{---------------------}(2)$$

Mark-Houwink Equation

K and a are constants,

Substituting (2) in (1) and solving the resulting expression for $\log M_X$, (3) is obtained

$$\log M_X = (1/(1+ax))\log (K_S/K_X) + \{(1+a_S)/(1+a_X)\}\log M_s \text{--------------------------}(3)$$

Obtain the elution volume V_e for the unknown polymer from GPC and look for the corresponding $\log M_S$ value from the calibration curve. M_X is then determined from (3).