Polymer Molecular weight and its Measurement methods

At the end of this lecture, you should be able to:

- Understand the distribution of polymer M.wt.
- Learn the ways to present the average M.wt
- Understand the measurement methods of polymer average M.wt.
- Calculate polymer average M.wt using different formula.

Molecular Weight:

Molecular weight of a chemical compound can be defined, simply, as the sum of the atomic weights of each of the atoms in the molecule.

Examples:

Water (H_2O) is 2 H (1g) and one O (16g) = 2*(1) + 1*(16)= 18 g/mol
Methane CH_4 is 1 C (12g) and 4 H (1g)= 1*(12) + 4 *(1) = 16 g/mole
Polyethylene -(C_2H_4)-$_{1000}$ = 2 C (12g) + 4H (1g) = 28g/mole * 1000 = 28,000 g/mole

Average Molecular Weight

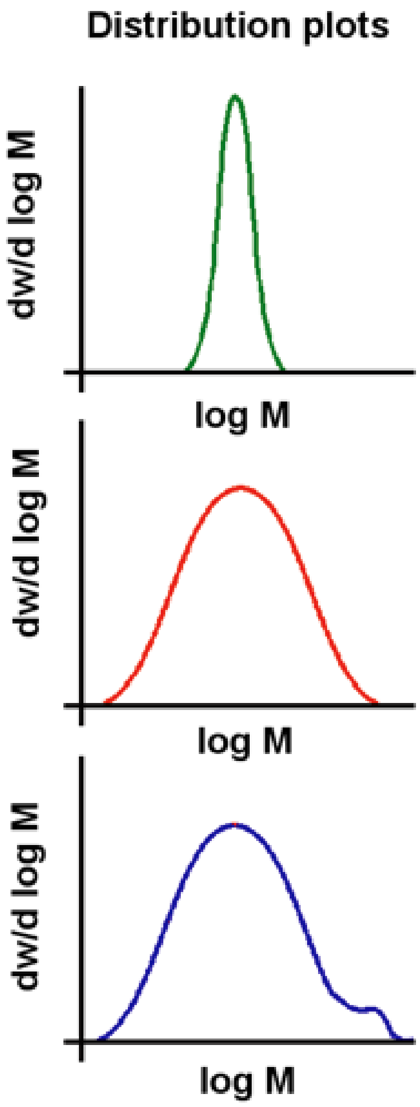
Polymers are made up of many molecular weights or a distribution of chain lengths. In other other words, if one takes polyethylene as an example, this polymer may have chains of ethylene (C_2H_4) with different lengths; some longer than others.

Example:

Polyethylene -(C_2H_4)-$_{1000}$ has some chains with 1001 repeating ethylene units, some with 1010 ethylene units, some with 999 repeating units, and some with 990 repeating units. The average number of repeating units or chain length is 1000 repeating ethylene units for a molecular weight of 28*1000 or 28,000 g/mole .

Therefore, polymers must be represented by the value of average molecular weight.

- Even for the same type of polymer, each of these distributions will describe a polymer that behaves differently
- The red and green plots are for low and high polydisperity materials
- The blue plot shows a high polydispersity material with a additional high molecular weight component
- Describing these distributions is not easily, especially if they are complex



There are four ways to represent the average molecular weight:

(1) ***Number-average molecular weight (Mn)*** for a discrete distribution of molecular weights is given as:

$$\bar{M}_n = \frac{\sum_{i=1}^{N} N_i M_i}{\sum_{i=1}^{N} N_i} = \frac{\sum_{i=1}^{N} W_i}{\sum_{i=1}^{N} (W_i / M_i)}$$

where *Ni* indicates the number of moles of molecules having a molecular weight of *Mi and Wi*, is the weight of molecules with molecular weight *Mi. Thus, Wi* = *Ni Mi*.

The expression for the number-average molecular weight of a continuous distribution function is:

$$\bar{M}_n = \frac{\int_0^\infty NM\,dM}{\int_0^\infty N\,dM}.$$

(2) ***Weight-average molecular weight (Mw)*** for a discrete distribution of molecular weights is given as:

$$\bar{M}_w = \frac{\sum_{i=1}^{N} N_i M_i^2}{\sum_{i=1}^{N} N_i M_i} = \frac{\sum_{i=1}^{N} W_i M_i}{\sum_{i=1}^{N} W_i}$$

The expression for the weight-average molecular weight of a continuous distribution function is:

$$\bar{M}_w = \frac{\int_0^\infty N M^2 dM}{\int_0^\infty N M dM}.$$

(3) ***Z-average molecular weight (Mz)*** for a discrete distribution of molecular weights is given as:

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

(4) *Viscosity-average* molecular weight (*M*v) can be obtained, experimentally, from dilute-solution viscometer using Mark-Howink equation. The viscosity-average molecular weight falls between *M*n and *M*w depending upon whether the solvent is a good or poor solvent for the polymer. In the case of a good solvent, *M*v = *M*w .

- Mark-Howink-Sakurada equation:

$$[\eta] = K\overline{M}^{a}$$

$[\eta]$: intrinsic viscosity
K , a : constant for specific polymer and solvent
$\overline{M}$: average molecular weight

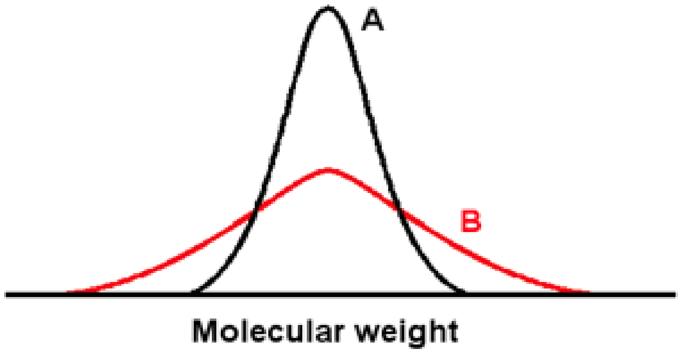
NOTES:

1. A measure of the breadth of the molecular-weight distribution is given by the ratios of molecular-weight averages. For this purpose, the most commonly used ratio is *M*w/*M*n ,called the *polydispersity index* or *PDI*.

$$PDI = \frac{Mw}{Mn} > 1$$; polymers having PDI = 1 are called monodiseperse polymers

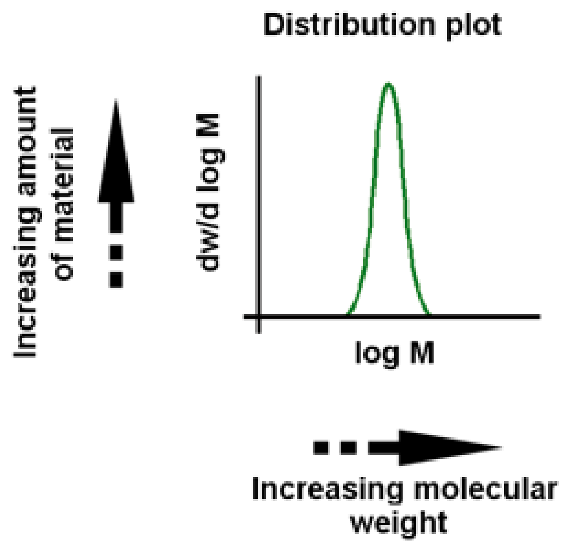
2. Degree of Polymerization (*DP*): is the number of monomeric units in a macromolecule or **polymer** or oligomer (consists of a few repeating units Or *DP* is the number of repeat units.

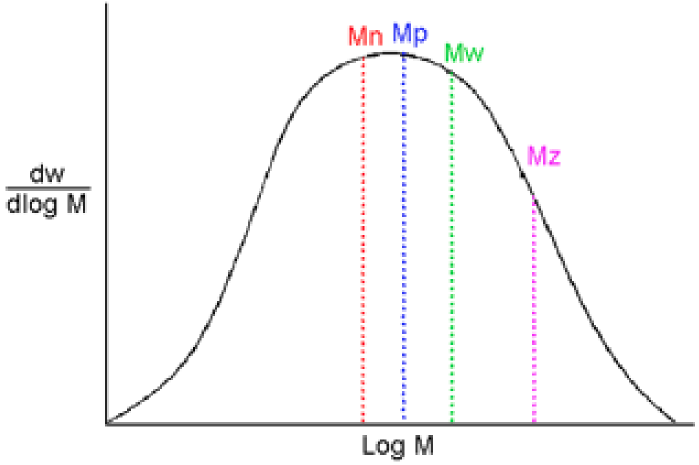
$$DP_w = \frac{Mw}{Mo} \quad , DP_n = \frac{Mn}{Mo}$$; where M_0 is the monomer molecular weight.



- As the broadness of the the distribution decreases the strength and toughness of the polymer increases
- However as the broadness of the the distribution decreases the polymer becomes more difficult to process

	Strength	Toughness	Brittleness	Melt viscosity	Chemical resistance	Solubility
Increasing Mw	+	+	+	+	+	-
Decreasing distribution	+	+	-	+	+	+





- A molecular weight distribution can be defined by a series of average values
- Except Mp, these are various moments of the average of the molecular weights of the distribution
- Mp is the molecular weight of the peak maxima
- For any polydisperse peak:

$$Mn < Mw < Mz$$

There are several reasons why we might want to measure polymer average molecular weight and its distribution:

1. The molecular weight and its distribution determine the viscous and elastic properties of the molten polymer. This affects the processibility of the melt and also the behavior of the resulting solid material. For example, a resin suitable for extrusion must have a high viscosity at low shear rates so that the extrudate maintains its integrity. To be suitable for injection molding, however, the same resin must have a low viscosity at high shear rates so that the injection pressure not be excessive.

2. The molecular weight of a polymer can determine its applications. For example, the resin used for making polycarbonate water bottles, for example, differs significantly in molecular weight from the polycarbonate that goes into compact disks.

3. Differences in molecular weight distribution also influence the polymer properties. As a consequence, two chemically similar polymers, processed identically, that have the same molecular weight but different molecular-weight distributions may result in products that show significantly different shrinkages, tensile properties, and failure properties. For this very important reason, it is advantageous to know the molecular weight and molecular-weight distribution of the polymers used.

4. Other situations where the molecular weight and its distribution directly influence results include phase equilibrium and crystallization kinetics.

Example 2.1:

A polydisperse sample of polystyrene is prepared by mixing three *monodisperse* samples in the following proportions:
1 g 10,000 molecular weight
2 g 50,000 molecular weight
2 g 100,000 molecular weight

Using this information, calculate the number-average molecular weight, weight- average molecular weight, and PDI of the mixture.

Solution:

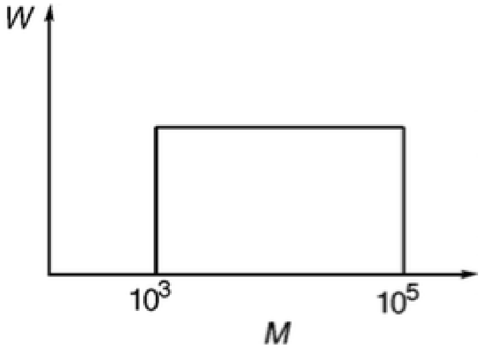
$$\bar{M}_n = \frac{\sum_{i=1}^{3} N_i M_i}{\sum_{i=1}^{3} N_i} = \frac{\sum_{i=1}^{3} W_i}{\sum_{i=1}^{3} \left(W_i / M_i\right)} = \frac{1+2+2}{\frac{1}{10,000}+\frac{2}{50,000}+\frac{2}{100,000}} = 31,250$$

$$\bar{M}_w = \frac{\sum_{i=1}^{3} N_i M_i^2}{\sum_{i=1}^{3} N_i M_i} = \frac{\sum_{i=1}^{3} W_i M_i}{\sum_{i=1}^{3} W_i} = \frac{10,000+2\left(50,000\right)+2\left(100,000\right)}{5} = 62,000$$

$$\mathrm{PDI} = \frac{\bar{M}_w}{\bar{M}_n} = \frac{62,000}{31,250} = 1.98$$

Example 2.2:

A polymer is fractionated and is found to have the continuous molecular-weight distribution shown below as a plot of the weight, *W*, of molecules having molecular weight, *M*, versus *W*. Given this molecular-weight distribution, calculate *M*n and *M*w.

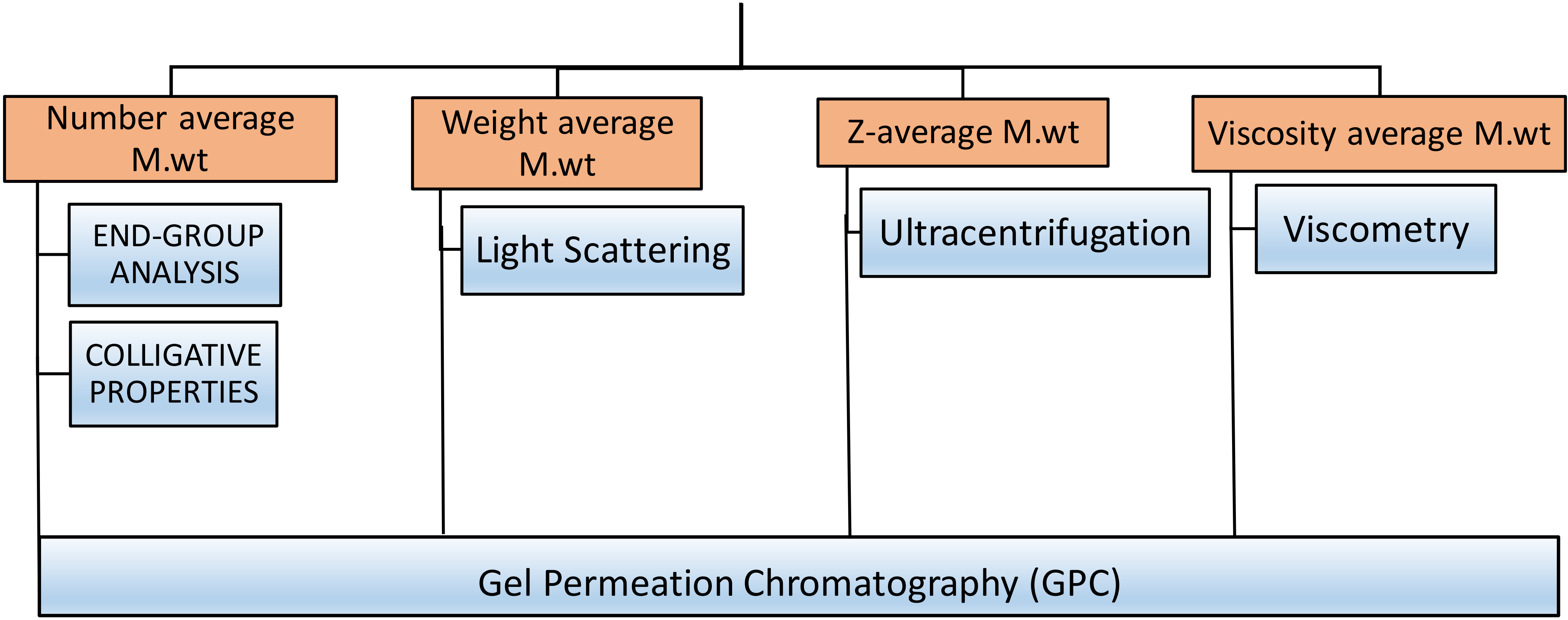


Solution:

$$\bar{M}_n = \frac{\int_{10^3}^{10^5} dM}{\int_{10^3}^{10^5} (1/M)\, dM} = \frac{10^5 - 10^3}{\ln\left(10^5/10^3\right)} = 21,498$$

$$\bar{M}_w = \frac{\int_{10^3}^{10^5} M dM}{\int_{10^3}^{10^5} dM} = \frac{\left(M^2/2\right)_{10^3}^{10^5}}{9.9\times 10^4} = 50,500$$

M.wt Measurement Methods



Number average M.wt

END-GROUP ANALYSIS

COLLIGATIVE PROPERTIES

Weight average M.wt

Light Scattering

Z-average M.wt

Ultracentrifugation

Viscosity average M.wt

Viscometry

Gel Permeation Chromatography (GPC)

NOTE: The choice of method for polymer molecular weight determination is influenced by factors such as: (i) information required, (ii) operative region, (iii) cost effectiveness, and (iv) experimental conditions and requirements.

End-group Analysis

This method has presumed importance particularly in the determination of average molecular weight of step-growth polymers (condensation). Consider the step-wise condensation polymerization of polyesters:

$$\begin{aligned} &\mathrm{nHOOC - R - COOH + nHO - R^1 - OH} \\ &\qquad \rightarrow \mathrm{HOOC - R - CO[-O - R^1 - O - CO - R - CO]_{n-1} - O - R^1 - OH + (n-1)H_2O} \end{aligned}$$

Under the assumption that each polymer chain contains one – OH and one – COOH groups, direct measurement of the concentration of the groups can be done using chemical (titrimetric or pH measurement) or spectroscopic (infrared or nuclear magnetic) techniques. This is also applicable to other step-growth polymers.

LIMITATIONS:

1. The major setback of this technique is the decrease in sensitivity with increasing polymer chain length. This method is restricted to polymer with molecular weight 20,000 amu. Aside this, it requires high concentration of polymer.
2. This method requires that the polymer be free of impurities and other groups present in the chain should not interfere in the determination of end group of interest.

colligative properties

The relations between the colligative properties and molecular weight for infinitely dilute solutions in a fact that the activity of the solute in a solution becomes equal to its mole fraction as the solute concentration becomes sufficiently small.

This method is based on:

- Vapour-pressure lowering,
- Boiling-point elevation (ebulliometry),
- Freezing-point depression (cryoscopy),
- Osmotic pressure (osmometry).

Formula Used

$$\left(\frac{\Delta T_b}{C}\right)_{C=0} = \frac{RT^2}{\rho \Delta H_v \overline{M}_n} + A_2C$$

$$\left(\frac{\Delta T_f}{C}\right)_{C=0} = \frac{RT^2}{\rho \Delta H_f \overline{M}_n} + A_2C$$

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

where

ΔTb, *ΔTf*, and *π* are the boiling-point elevation, freezing-point depression, and osmotic pressure, respectively.

ρ is the density of the solvent,

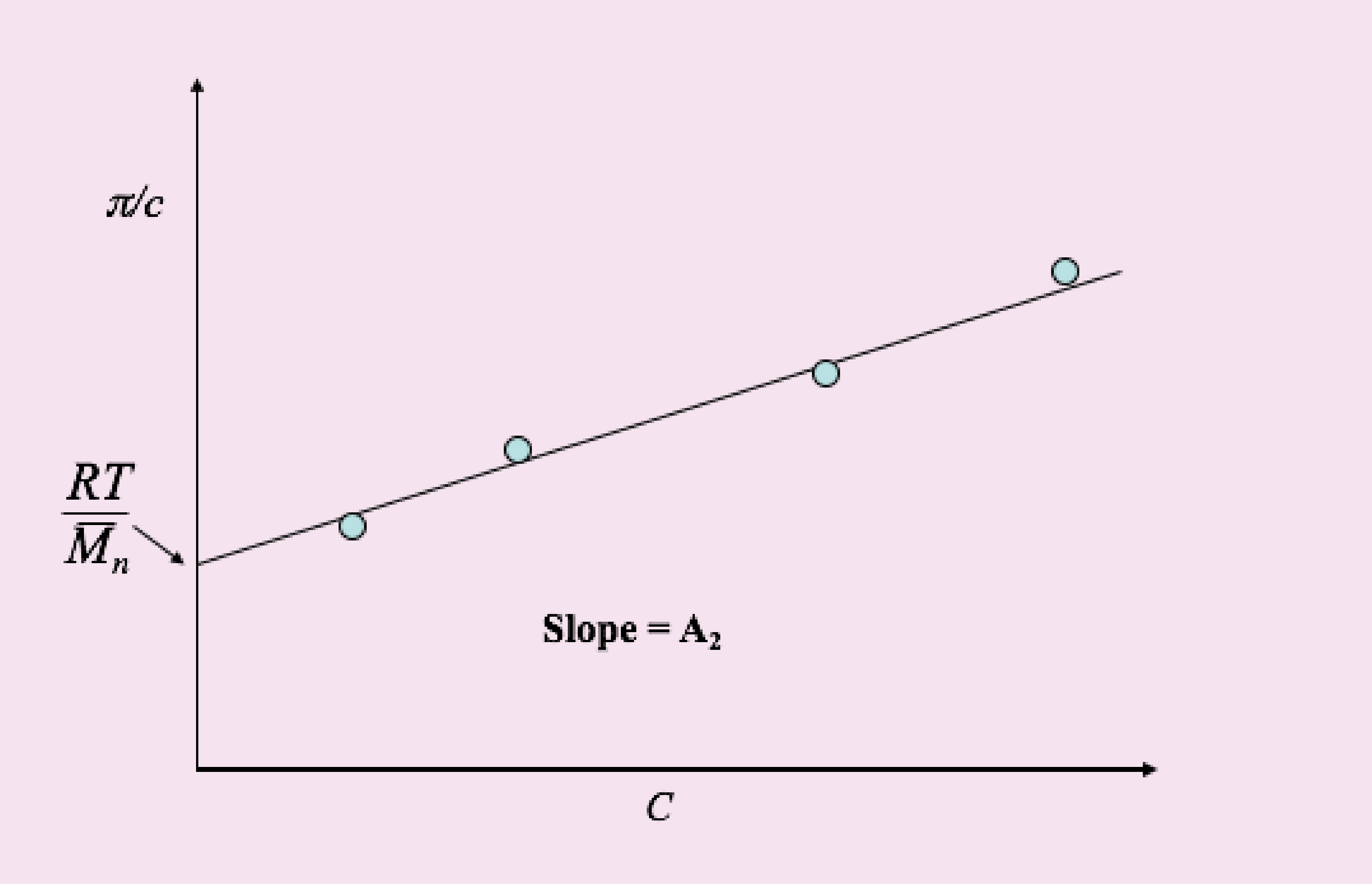
ΔHv and *ΔHf* are the enthalpies of vaporization and fusion, respectively, of the solvent per gram,

c is the solute concentration (gr/cm3),

Mn is the number-average molecular weight.

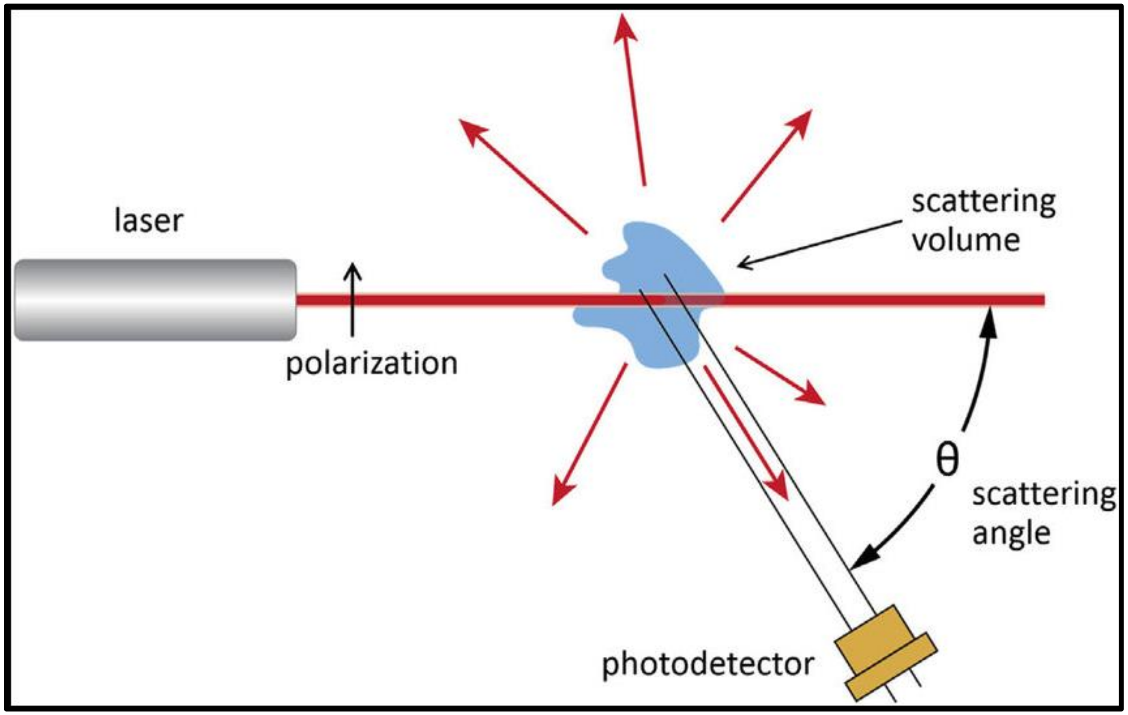
A2 is a constant.

An example of determining *Mn* from vapour pressure data



Light Scattering

This method is presumed most popular for the determination of weight average molecular weight (Mw). It allows polymer molecular weight and structure to be assessed. Fundamentally, if light passes through a medium, it scatters at different angles. This technique thus relies on the measurement of light scattered at an angle to the incident ray as it passes through the target. The intensity of scattered light incident on polymer sample is dependent of **the polarity, chain size, and concentration**. Consequent upon this, light technique measures polymer molecular weight by quantifying the Raleigh scattering (elastic light scattering) from each polymer molecule. The measurement approach is simple as illustrated in the Figure below.



The famousness of this method stems from the fact that wide range of molecular weight (typically 10^4 to 6×10^5 g/mol) can be determined.

The scattered light and the average molecular weight is related according to the following equation:

$$\Delta R_\theta = Kc\overline{M}_w \overline{P(\theta)_z}$$

where ΔR_θ is the change in Raleigh scattering at a specified angle, K is the optical constant, C is the polymer concentration, and $\overline{P(\theta)_z}$ is the average particle scattering factor which accounts for the effects of measuring scattering from large molecules with relatively small wavelength.

LIMITATIONS:

However, the light scattering technique is deemed time consuming because it requires that the sample solution is completely free of dust and other impurities as these are capable of influencing the light scattering pattern. Also, as could be deduced from the above equation, change in Raleigh scattering is proportional to the sample concentration and molecular weight, hence this method requires high sample concentration to produce a detectable signal.

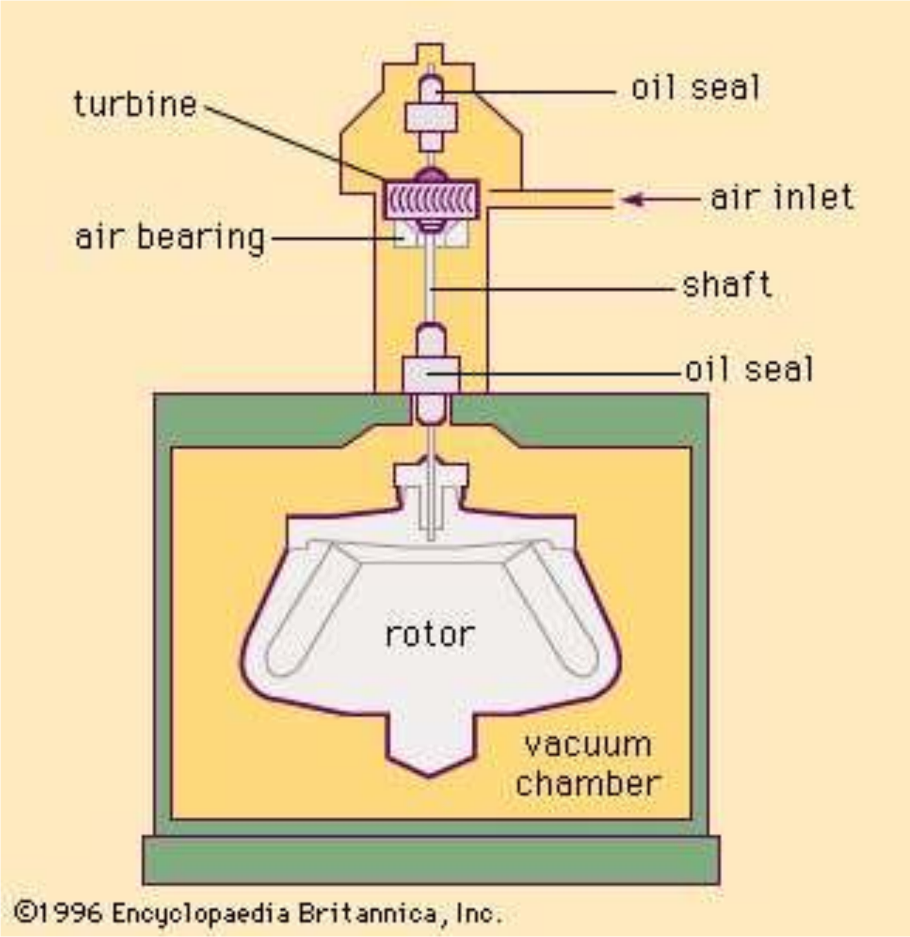
Ultracentrifugation (Sedimentation) Method

It is the most intricate of the methods for determining the molecular-weights of high polymers. This method is useful for biological materials, such as protein molecules.

An ultracentrifuge consists of an AL rotor (ø ~1-2 inch) that is rotated at high speed in an evacuated chamber. The solution being centrifuged is held in a small cell within the rotor near its periphery. The rotor is driven electrically or by oil or air turbine.

The concentration of polymer is determined by optical methods based on measurements of refractive index or absorption. The solvents must have difference both density and refractive index from the polymer. The density differences allow the sedimentation and the refractive index differences allow the measurement.

In the sedimentation equilibrium experiment, the ultracentrifuge is operated at a low speed of rotation for times up 1 or 2 weeks under constant conditions. A thermodynamic equilibrium is reached in which the polymer is distributed in the cell according to its molecular weight and molecular-weight distribution.



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https://www.britannica.com/technology/ultracentrifugation

The force on a particle (F):

$$F = \omega^2 r(1-\upsilon\rho)m$$

where:
ω is the angular velocity of rotation,
r is the distance of the particle from the axis of rotation,
υ is the partial specific volume of the polymer,
ρ is the density of the solution,
m is the mass of the particle.

For an ideal solution in the equilibrium condition:

$$\overline{M}_w = \frac{2RT\ln\left({}^{c_2}\!/_{c_1}\right)}{(1-\overline{\upsilon}\rho)\omega^2\left(r_2^2-r_1^2\right)}$$

where: c1 and c2 are the concentrations at 2 points r1 and r2 in the cell.

<u>**LIMITATIONS:**</u> The disadvantage of sedimentation equilibrium experiment is taking quite long time to reach equilibrium.

Ultracentrifugation Method

Example: At rotation rate 400 rpm (41.8 m/s) and 20 ^{o}C, the concentration ratio (C2/C1) is 1000. If the r_2 and r_1 are 5 cm and 10 cm , respectively, the density is 1 gm/cm3 and the partial specific volume of the polymer is 0.0077 cm^3/gm, what is the molecular weight.

SOLUTION:

$$\overline{M}_w = \frac{2RT\ln\left({}^{c_2}\!/\!{}_{c_1}\right)}{\left(1-\bar{\upsilon}\rho\right)\omega^2\left(r_2^2-r_1^2\right)}$$

$$\mathrm{Mw} = \frac{(2)(8.314)(293)\ln(1000)}{(1-0.0077*1)(41.8)^2\ ((0.1)^2-(0.05)^2)}$$

$$\mathrm{Mw} = 2587.8\ gm/mole$$

Viscometry

A method that is widely use for routine molecular-weight determination is based on the determination of intrinsic viscosity, η, of a polymer in solution through measurements of solution viscosity.

The fundamental relationship between η and molecular-weight is given in Mark-Howink equation (mentioned in Page 6):

$$[\eta] = K\overline{M}^a$$

$[\eta]$: intrinsic viscosity
K , a : constant for specific polymer and solvent
$\overline{M}$: average molecular weight

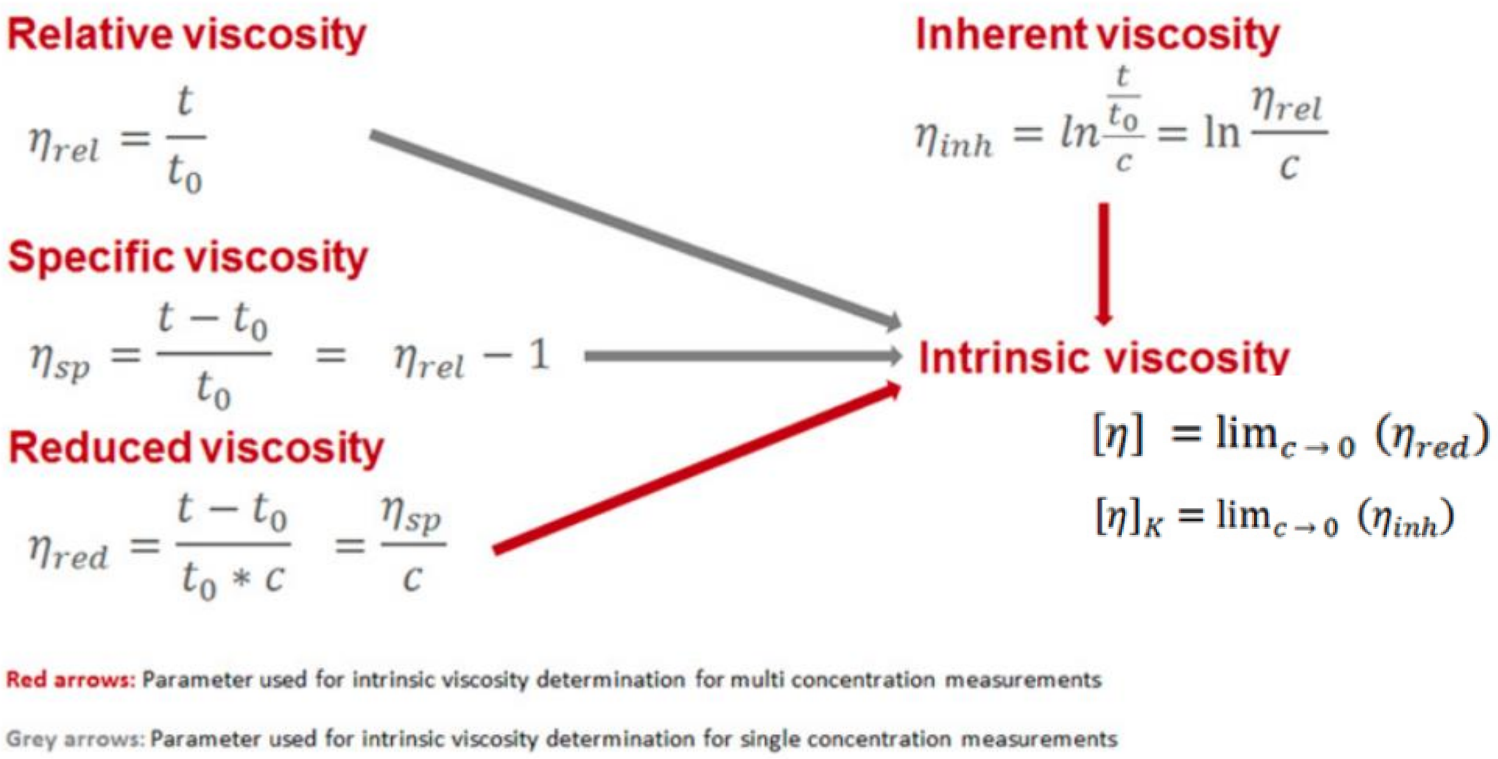
It is clear in the above equation that the value of intrinsic viscosity of the diluted polymer is needed to determine the molecular weight. To find the intrinsic viscosity, a series of experimental measurements and calculations have to be made. These steps are as follows:

1. The relative viscosity can be measured experimentally using a suitable viscometer:

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

η : solution viscosity
η_o: solvent viscosity
t : flow time of solution
t_o: flow time of solvent

2. The intrinsic viscosity can be calculated as shown below:



Relative viscosity

$$\eta_{rel} = \frac{t}{t_0}$$

Specific viscosity

$$\eta_{sp} = \frac{t - t_0}{t_0} = \eta_{rel} - 1$$

Reduced viscosity

$$\eta_{red} = \frac{t - t_0}{t_0 * c} = \frac{\eta_{sp}}{c}$$

Inherent viscosity

$$\eta_{inh} = ln\frac{\frac{t}{t_0}}{c} = \ln\frac{\eta_{rel}}{c}$$

Intrinsic viscosity

$$[\eta] = \lim_{c \to 0} (\eta_{red})$$

$$[\eta]_K = \lim_{c \to 0} (\eta_{inh})$$

Red arrows: Parameter used for intrinsic viscosity determination for multi concentration measurements

Grey arrows: Parameter used for intrinsic viscosity determination for single concentration measurements

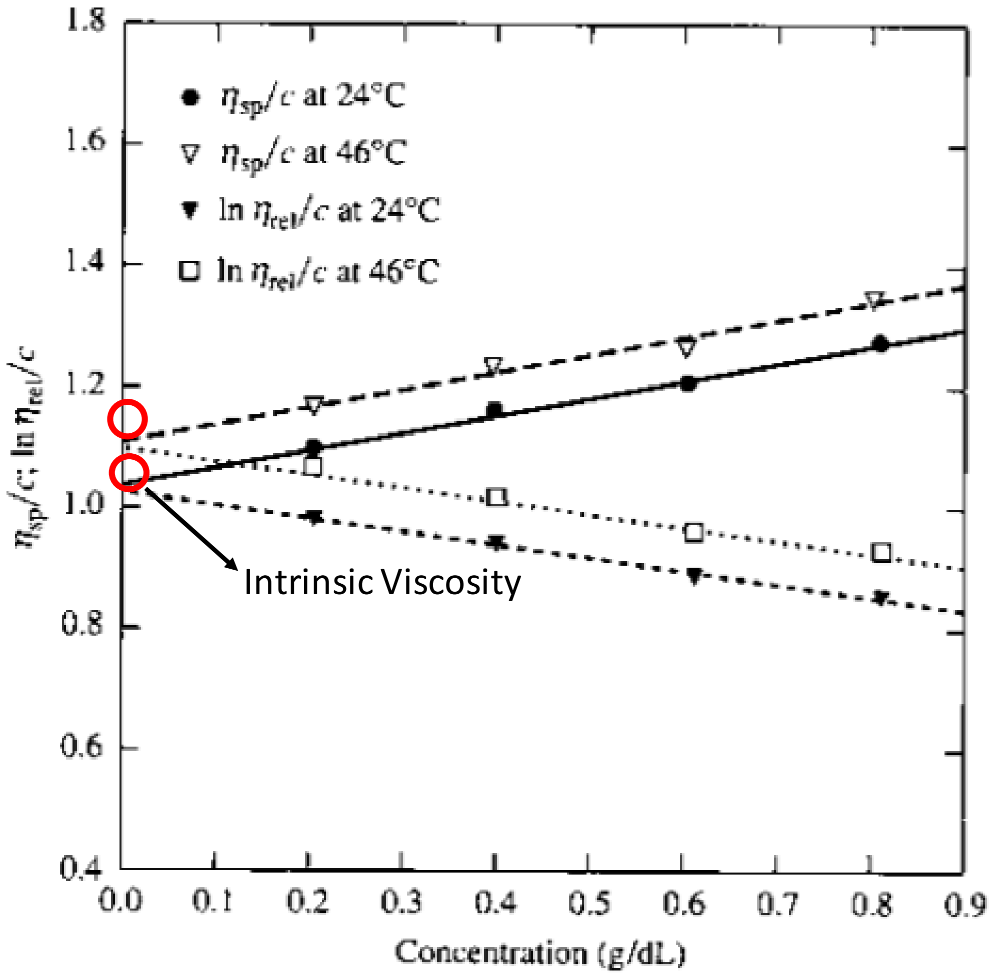
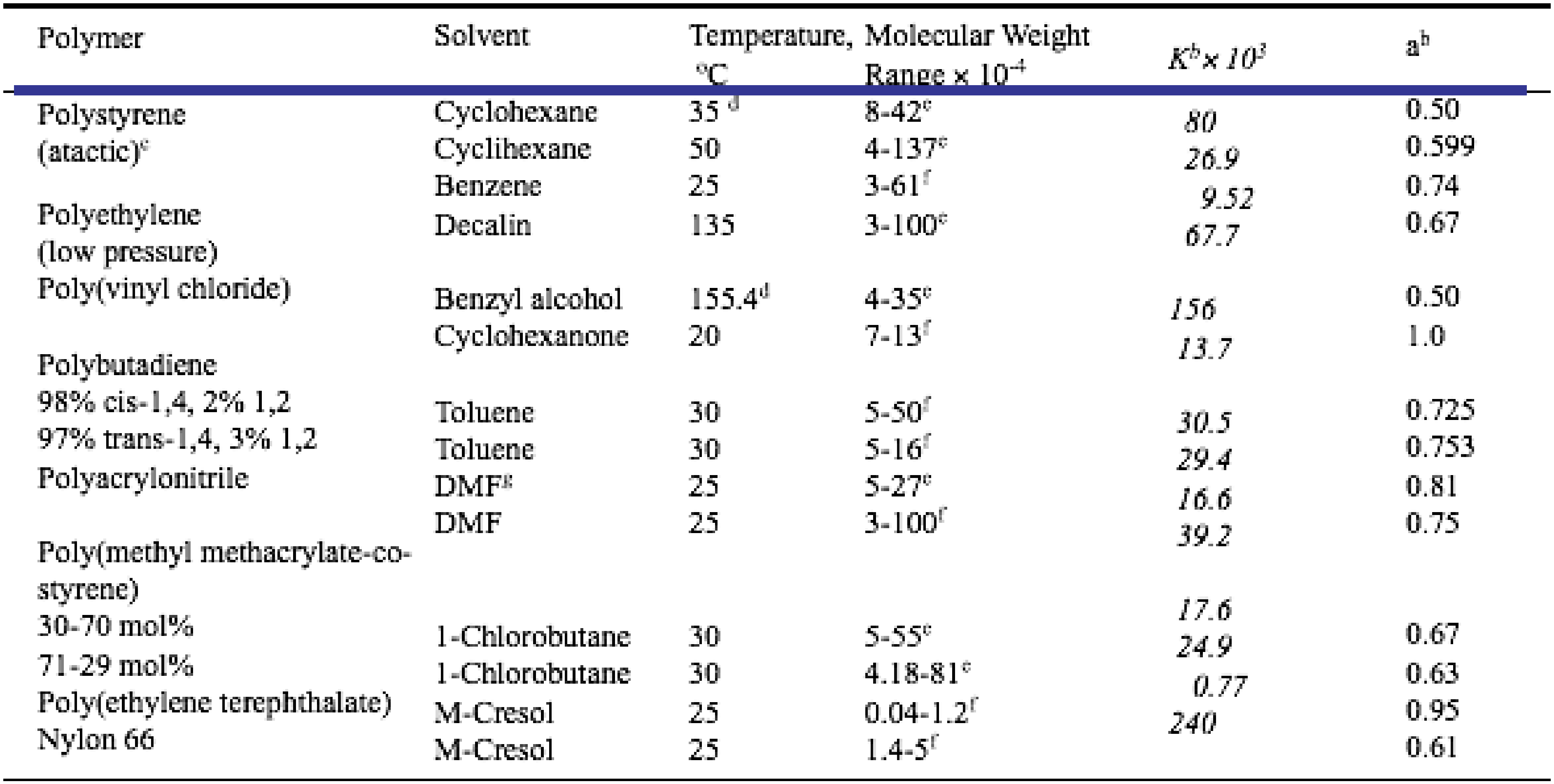


Fig. 1 Reduced viscosity and inherent viscosity of nylon 66 in 90% formic acid (Adapted from Ph.D thesis of R Walia, P. S., Chemical Engineering, West Virginia University, Morgantown, 1998).

Viscosity-Molecular Weight Constants



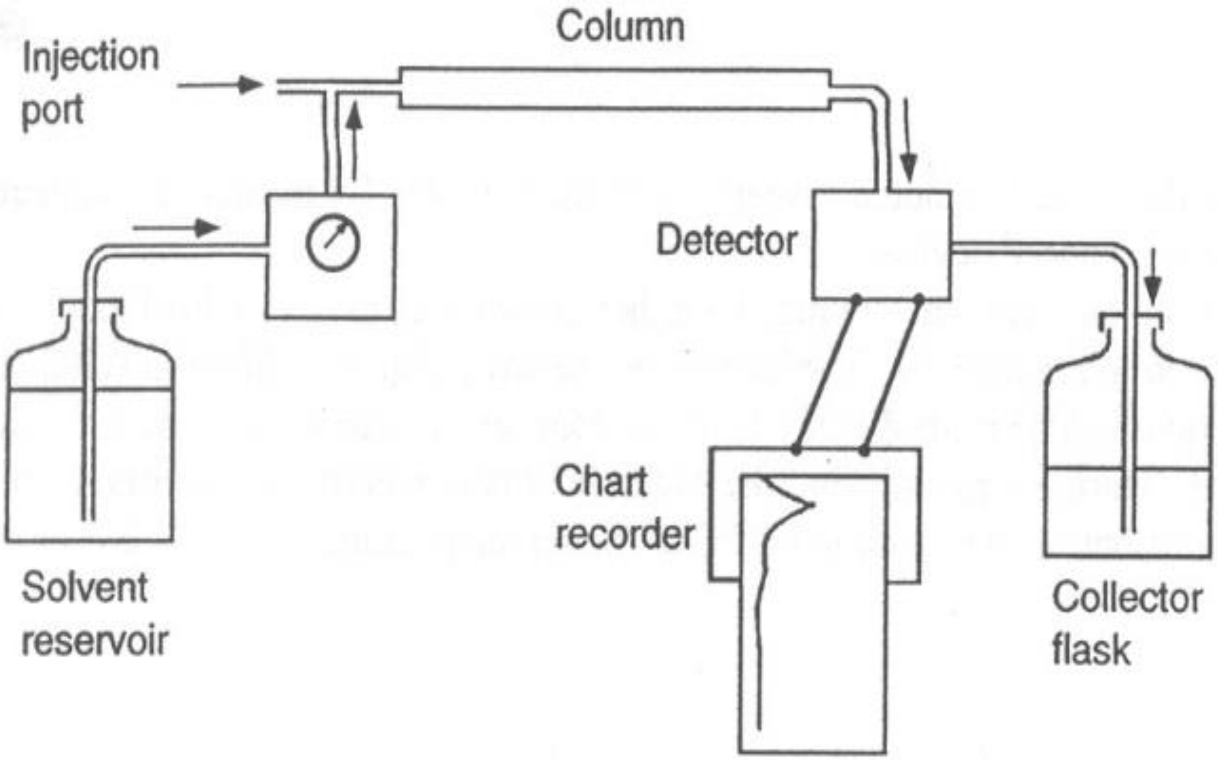
Polymer	Solvent	Temperature, °C	Molecular Weight Range × 10^{-4}	$K^b \times 10^3$	a^b
Polystyrene (atactic)^c	Cyclohexane	35 ^{d}	8-42^e	80	0.50
	Cyclihexane	50	4-137^e	26.9	0.599
	Benzene	25	3-61^f	9.52	0.74
Polyethylene (low pressure)	Decalin	135	3-100^e	67.7	0.67
Poly(vinyl chloride)	Benzyl alcohol	155.4^d	4-35^e	156	0.50
	Cyclohexanone	20	7-13^f	13.7	1.0
Polybutadiene					
98% cis-1,4, 2% 1,2	Toluene	30	5-50^f	30.5	0.725
97% trans-1,4, 3% 1,2	Toluene	30	5-16^f	29.4	0.753
Polyacrylonitrile	DMF^g	25	5-27^e	16.6	0.81
	DMF	25	3-100^f	39.2	0.75
Poly(methyl methacrylate-co-styrene)					
30-70 mol%	1-Chlorobutane	30	5-55^e	17.6	0.67
71-29 mol%	1-Chlorobutane	30	4.18-81^e	24.9	0.63
Poly(ethylene terephthalate)	M-Cresol	25	0.04-1.2^f	0.77	0.95
Nylon 66	M-Cresol	25	1.4-5^f	240	0.61

Gel Permeation Chromatography (GPC)

One of the most widely used methods for routine determination of molecular weight and molecular-weight distribution is GPC. This method based on the principle of size-exclusion chromatography to separate samples of polydisperse polymers into fractions of narrower molecular-weight distribution.

The equipment:
Several small-diameter columns (L = 30 – 50 cm) are packed with small highly porous beads (Ø = 10 – 107 Â).
Pure pre-filtered solvent is continuously pumped through the columns at a constant flow rate
(1 – 2 mL/min). Then, a small amount (1 – 5 mL) of a dilute polymer solution is injected by syringe into the solvent stream and carried through the columns. The smallest polymer molecules are able to penetrate deeply into the bead pores but the largest may be completely excluded.

The process is repeated until all polymer molecules have been eluted out of the column in descending order of molecular weight. The concentration of polymer molecules in each eluting fraction can be monitored by means of a polymer-sensitive detector, such as IR or UV device. The detector is usually a differential refractometer (differ the refractive index between the pure solvent and polymer solution).
For a given polymer, solvent, temperature, pumping rate, and column packing size, elution volume (Vr) is related to molecular weight.


Column
Injection port
Detector
Chart recorder
Solvent reservoir
Collector flask

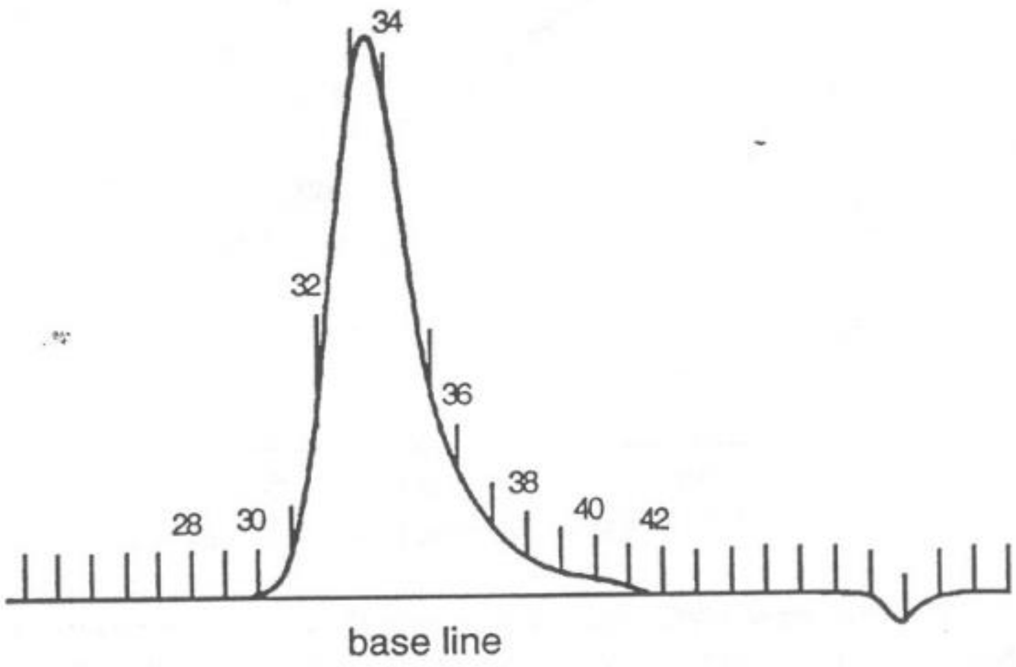
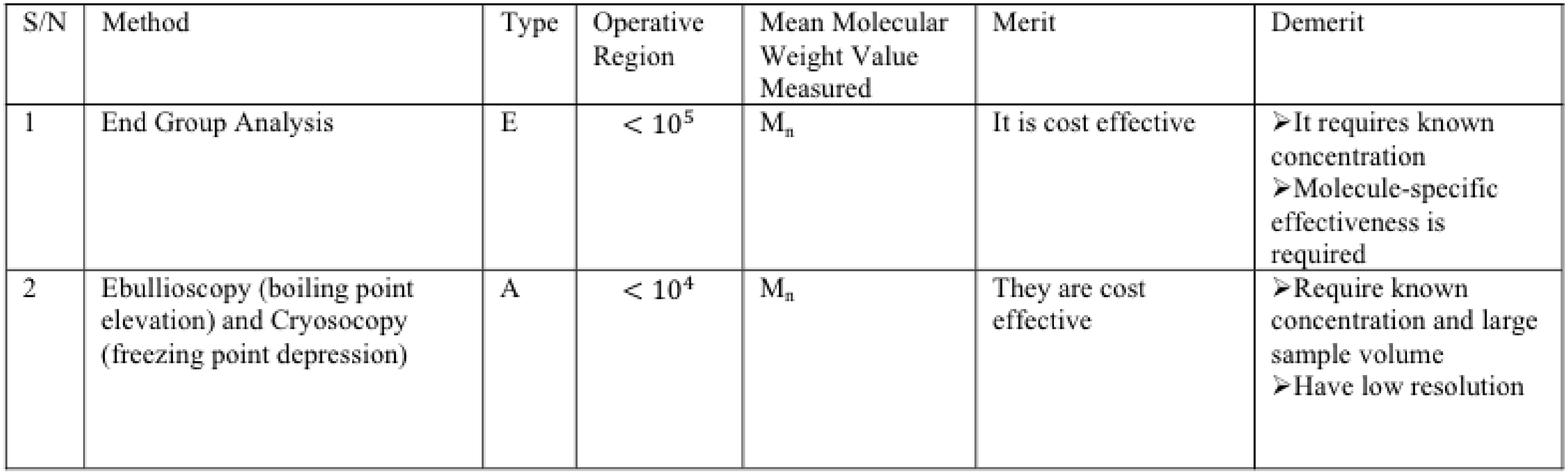


Figure 3.21. GPC chromatogram of a polystyrene sample using tetrahydrofuran as the solvent at a flow rate of 2.0 mL min^{-1}. Vertical marks represent elution counts. The highest-molecular-weight polymer molecules elute at the lowest elution counts (above ca. 29). The negative peak at high elution-volume is usually due to a low-molecular-weight impurity or impurities, such as traces of solvent, stabilizer, water, or dissolved air. (Adapted from L. H. Sperling, *Introduction to Physical Polymer Science*. Copyright ©1986. Reprinted by permission of John Wiley & Sons, Inc.)

Summary of the Measurements Method of M.wt

A = Absolute
E = Equivalent
R = Relative



S/N	Method	Type	Operative Region	Mean Molecular Weight Value Measured	Merit	Demerit
1	End Group Analysis	E	$< 10^5$	M_n	It is cost effective	➢It requires known concentration ➢Molecule-specific effectiveness is required
2	Ebullioscopy (boiling point elevation) and Cryosocopy (freezing point depression)	A	$< 10^4$	M_n	They are cost effective	➢Require known concentration and large sample volume ➢Have low resolution

3	Osmometry	A	$10^4 - 10^6$	M_n	It is cost effective	➢Requires known concentration ➢Is less efficient for high molecular weight determination
4	Gel Permeation Chromatography (GPC)	R	$10^2 - 10^7$	Different values	➢It measures wide range of molecular weight ➢It is sensitive and has high resolution ➢It can measure polydispersity	➢It uses semi-dilute solution ➢It requires known concentration ➢It is slow ➢The equipments are expensive ➢Sample solution is difficult to prepare
5	Light Scattering	A	$10^2 - 10^8$	M_w	It can measure polydispersity	➢It requires known concentration ➢Sample preparation is difficult
6	Sedimentation Equilibrium	A	$< 10^6$	M_w, M_z	It can measure polydispersity	➢It requires known concentration ➢Sample preparation is tedious
7	Viscometry	R	$10^2 - 10^8$	M_η	➢It is cost effective ➢It measures wide range of molecular weight	➢It requires known concentration ➢It shows low accuracy for low molecular weights