In most coordination polymers, a ligand (atom or group of atoms) will formally donate a lone pair of electrons to a metal cation and form a coordination complex via a Lewis acid/ base relationship (Lewis acids and bases). Coordination polymers are formed when a ligand has the ability to form multiple coordination bonds and act as a bridge between multiple metal centers.

Polymers in industry

Type	Abbreviation	Typical Uses
Phenol-formaldehyde	PF	Electrical and electronic equipment, automobile parts, utensil handles, plywood adhesives, particle board binder
Urea-formaldehyde	UF	Similar to PF polymer; also treatment of textiles, coatings
Unsaturated polyester	UP	Construction, automobile parts, boat hulls, marine accessories, corrosion-resistant ducting, pipe, tanks, etc., business equipment
Epoxy	-	Protective coatings, adhesives, electrical and electronics applications, industrial flooring highway paving materials, composites
Melamine-formaldehyde	MF	Similar to UF polymers; decorative panels, counter and table tops, dinnerware

Glass transition temperature

Collections of molecules can exist in three possible physical states: solid, liquid and gas. In polymeric materials, things are not so straightforward. For example, most polymers will decompose before they boil, and cross-linked polymers decompose before they melt. For many polymers the transition between the solid and liquid states is rather diffuse and difficult to pinpoint. Amorphous polymers are viscous liquids when they are held at temperatures above their glass transition temperature, Tg. Below Tg, the material is solid, yet has no long-range molecular order and so is non-crystalline. In other words, the material is an amorphous solid, or a glass. The glass transition temperature is different for each polymer, but many polymers are above Tg at room temperature. In many cases the polymers are at least partially crystalline at room temperature and the temperature at which the crystals melt (Tm) is above room temperature.

When an amorphous polymer is heated, the temperature at which the polymer structure turns "viscous liquid or rubbery" is called the Glass Transition Temperature, Tg. It is also defined as a temperature at which amorphous polymer takes on characteristic glassy-state properties like brittleness, **stiffness** and rigidity (upon cooling).

This temperature (measured in °C or °F) depends on the chemical structure of the polymer and can therefore be used to identify polymers.

Amorphous polymers only exhibit a Tg.
Crystalline polymers exhibit a Tm (melt temperature) and typically a Tg since there is usually an amorphous portion as well ("semi"-crystalline).

The value of Tg depends on the mobility of the polymer chain, and for most synthetic polymers lies between 170 K to 500 K.

The transition from the glass to the rubber-like state is an important feature of polymer behavior, marking a region of dramatic changes in the physical properties, such as **hardness** and elasticity.

The graph below shows how some polymers are above Tg but below Tm at room temperature. Such polymers are rubbers (so long as they are largely amorphous) at room temperature. However, the polymer may flow like a liquid over long time periods as its amorphous component relaxes under the polymer's weight.
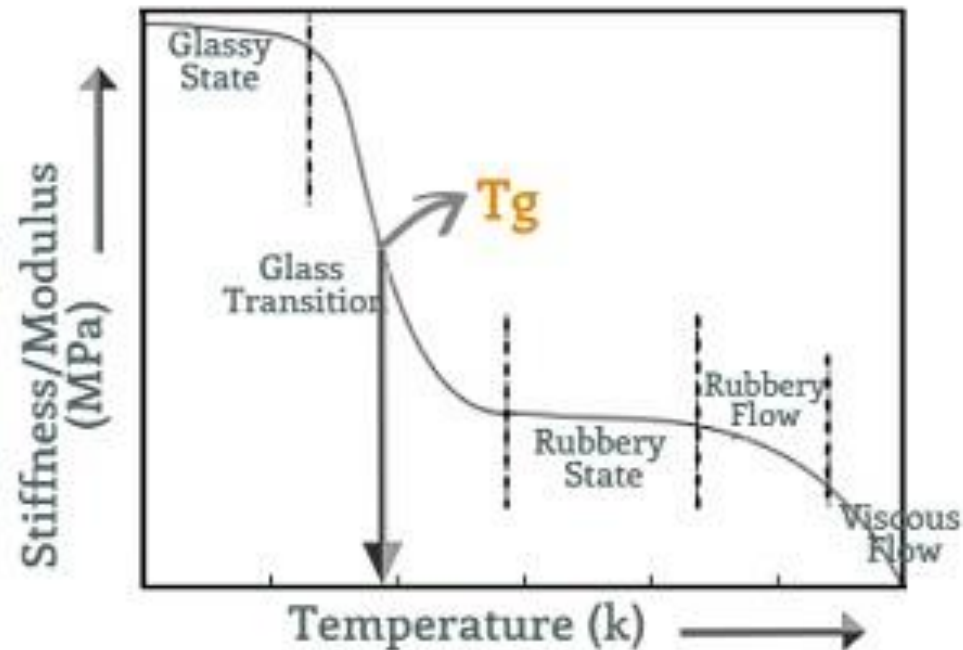
At Tg, changes in hardness, volume, percent **elongation to break** and **Young's modulus** of solids are mainly seen.

Some polymers are used below their Tg (in glassy state) like polystyrene, **poly(methyl methacrylate)** etc., which are hard and brittle. Their Tgs are higher than room temperature.

Some polymers are used above their Tg (in rubbery state), for example, rubber elastomers like polyisoprene, polyisobutylene. They are soft and flexible in nature; their Tgs are less than room temperature.

Applications include:
Identifying the Tg of polymers is often used for quality control and research and development. Also, it is an important tool used to **modify physical properties of polymer molecules.**

Further, improvement in handling characters, solubility and reproducibility in dissolution of solids can be achieved by increasing the Tg of solids.

The most usual test **method to determine Glass Transition Temperature** of plastics is **ASTM E1356**. This test method covers the assignment of the glass transition temperatures of materials using **differential scanning calorimetry** or **differential thermal analysis**.

This test method is applicable to amorphous materials or to partially crystalline materials containing amorphous regions, that are stable and do not undergo decomposition or sublimation in the glass transition region.

Both methods, DTA and DSC, yield peaks relating to endothermic and exothermic transitions with thermal input and show phase changes or occurrence of reactions.

In DTA, the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature rise/fall of the sample, in a specified atmosphere, is programmed.

In DSC, the difference in heat flow to a sample and to a reference is monitored against time or temperature while the temperature rise/fall of the sample, in a specified atmosphere, is programmed.
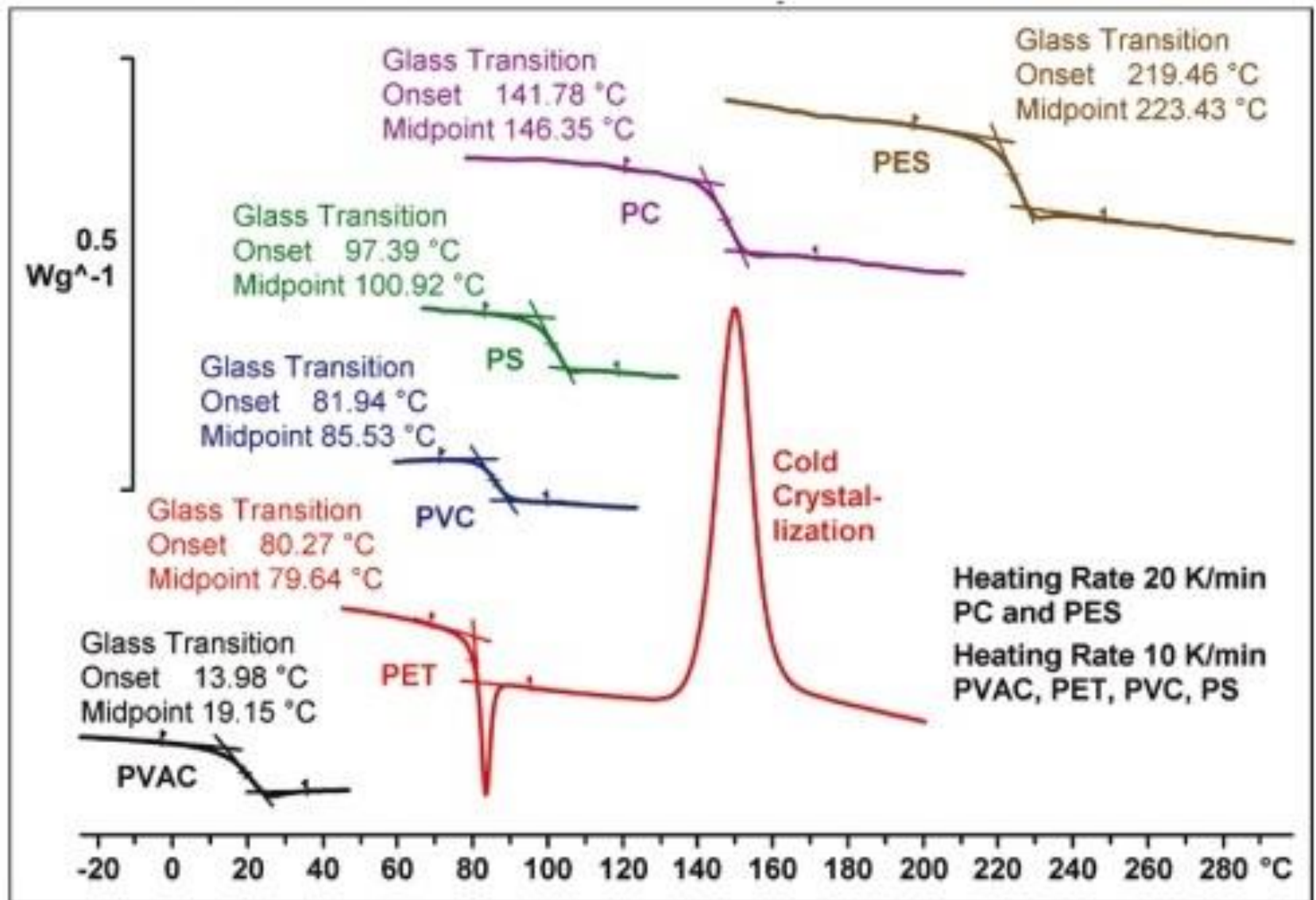
The operating temperature of polymers is defined by transition temperatures

At the molecular level, at Tg, the chains in amorphous (i.e., disordered) regions of the polymer gain enough thermal energy to begin sliding past one another at a noticeable rate. The temperature where entire chain movement occurs is called the melting point (Tm) and is greater than the Tg

Glass Transition is a property of the amorphous region while melting is the property of crystalline region

Below Tg, there exists disordered amorphous solid where chain motion is frozen and molecules start wiggling around above Tg. The more immobile the chain, the higher the value of Tg.

While, below Tm it is an ordered crystalline solid which becomes disordered melt above Tm.

The operating temperature of polymers is defined by transition temperatures

The glass transition of a polymer is related to the thermal energy required to allow changes in the conformation of the molecules at a microscopic level, and above Tg there is sufficient thermal energy for these changes to occur. However, the transition is not a sharp one, nor is it thermodynamically well defined. It is therefore different from melting a crystal. A distinct change from rubbery (above Tg) to glassy (below Tg) behaviour is readily observable in a wide range of polymers over a relatively narrow temperature range. It is necessary to explore the behaviour of polymers around the glass transition temperature and the effects of strain rate, cooling or heating rate and other factors affecting the glass transition temperature.

The temperature above which the torsion angles can change is called the glass transition temperature.

Factors affecting Tg:

- Chain Length- Each chain end has some free volume associated with it. A polymer with shorter chains will have more chain ends per unit volume, so there will be more free volume. Hence Tg' for shorter chains will be lower than Tg for long chains.

- Chain Flexibility- A polymer with a backbone that exhibits higher flexibility will have a lower Tg. This is because the activation energy for conformational changes is lower. Therefore, conformational changes can take place at lower temperatures.

- Side Groups- Larger side groups can hinder bond rotation more than smaller ones, and therefore cause an increase in Tg. Polar groups such as Cl, CN or OH have the strongest effect.

- Branching Polymers- with more branching have more chain ends, so have more free volume, which reduces T_g, but the branches also hinder rotation, like large side groups, which increases T_g. Which of these effects is greater depends on the polymer in question, but T_g may rise or fall.
- Cross-linking- reduces chain mobility, so T_g will be increased. It also affects the macroscopic viscosity of the polymer, since if there are cross-links between the chains, then they are fixed relative to each other, so will not be able to slide past each other.
- Plasticisers- Small molecules, typically esters, added to the polymer increase the chain mobility by spacing out the chains, and so reduce T_g.

- Time Effects- The properties of an amorphous polymer above Tg can change with time. At very short loading times the polymer can still be glassy because there is not time for the chains to move. At intermediate times the polymer may be rubbery- i.e. chains can uncoil and recoil between entanglements, which remain stable. At very long times, the chains can move past each other permanently, and so the polymer behaves as a viscous liquid.

Polymers-Tg

Dry Nylon-6 has a glass transition temperature of 47 °C. Nylon-6,6 in the dry state has a glass transition temperature of about 70 °C. Whereas polyethene has a glass transition range of −130 to −80°C.

It must be kept in mind that the above are only mean values, as the glass transition temperature depends on the cooling rate and molecular weight distribution and could be influenced by additives.

Note also that for a semi-crystalline material, such as polyethene that is 60–80% crystalline at room temperature, the quoted glass transition refers to what happens to the amorphous part of the material upon cooling.

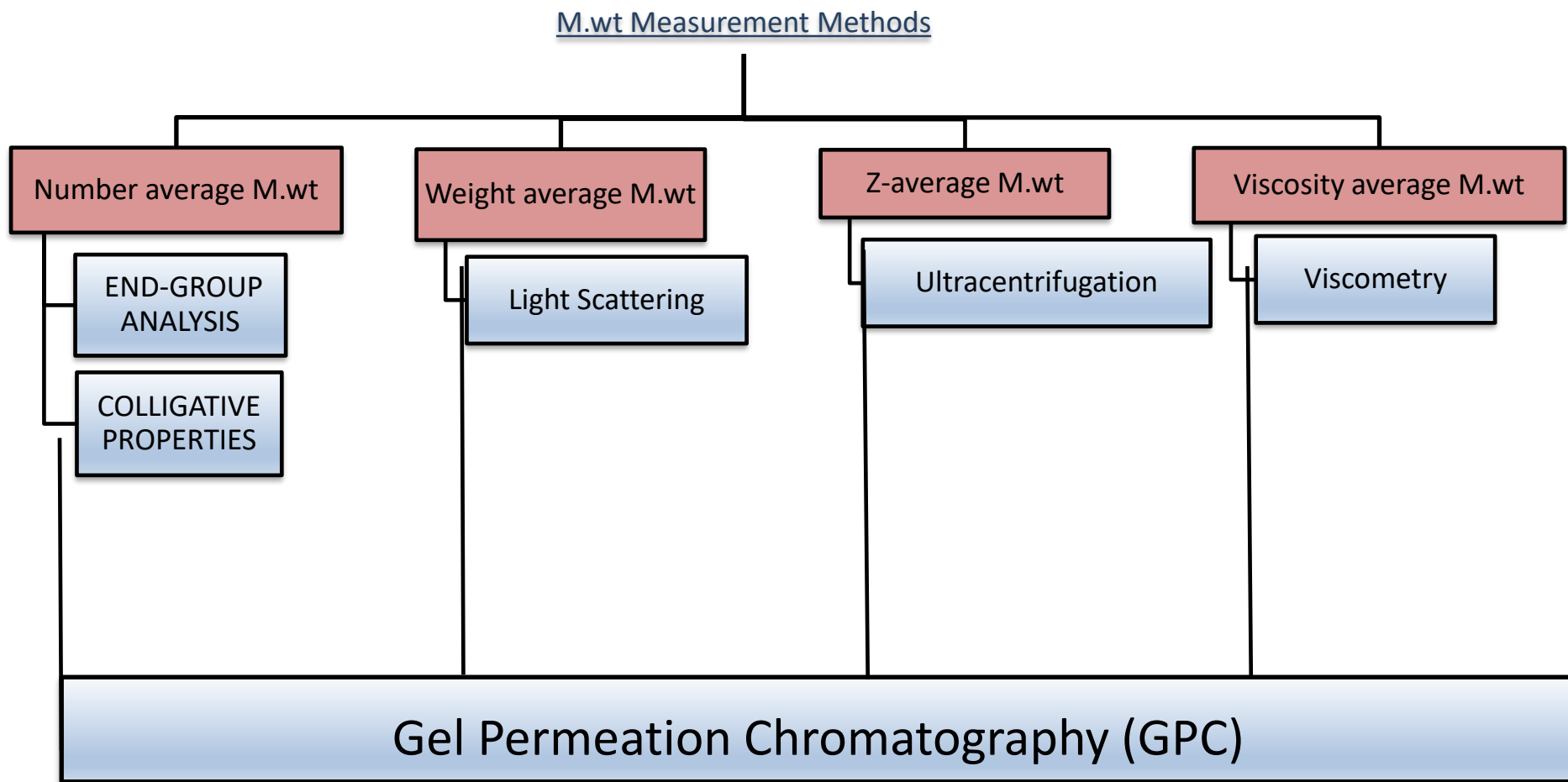Values of T_g and T_m for various polymers
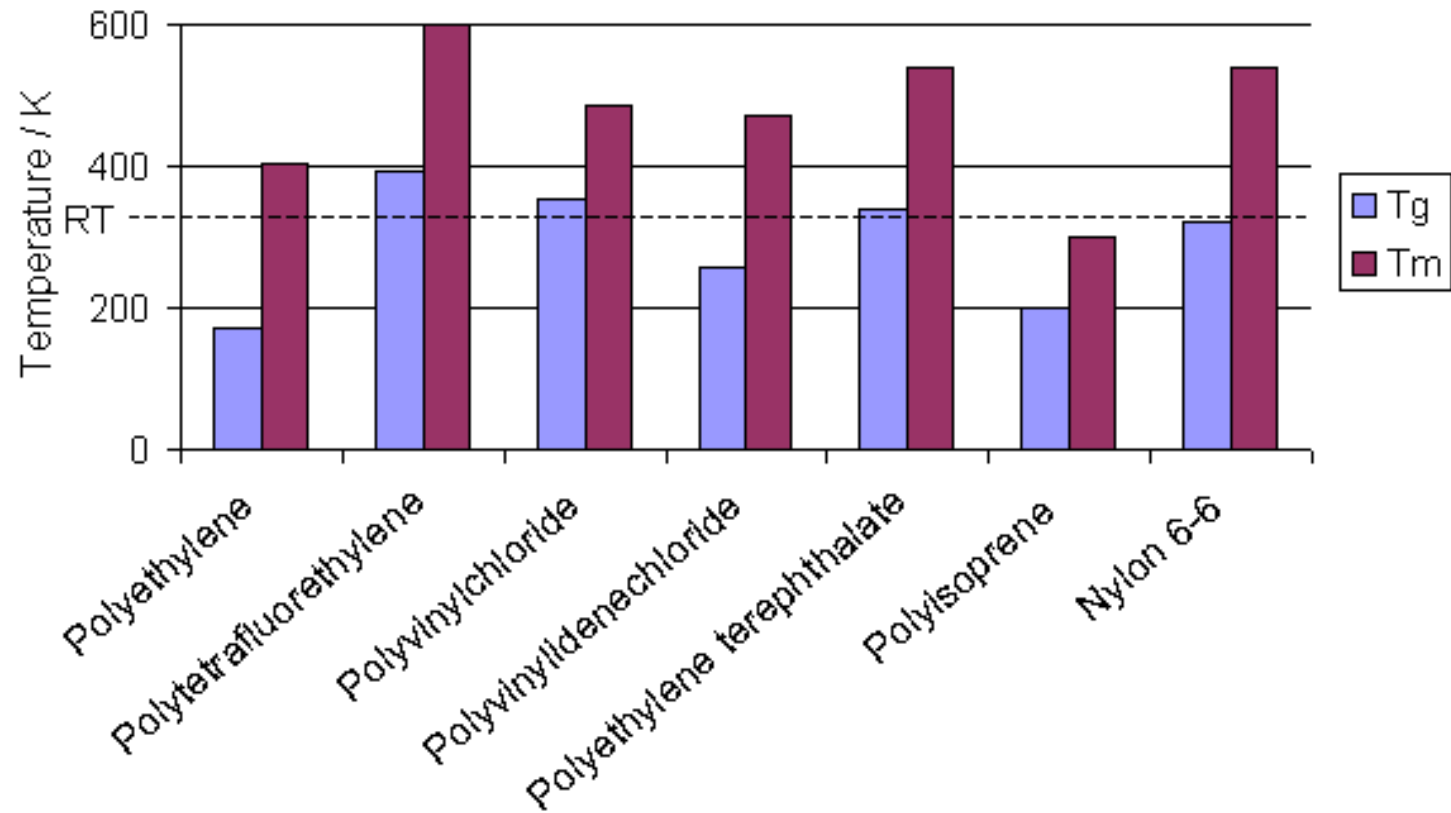
Polymer Molecular weight and its Measurement methods

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 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.

M.wt Measurement Methods

Number average M.wt	Weight average M.wt	Z-average M.wt	Viscosity average M.wt
END-GROUP ANALYSIS	Light Scattering	Ultracentrifugation	Viscometry
COLLIGATIVE PROPERTIES			

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.

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.

There are four ways to represent the average molecular weight:

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

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

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:

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

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:

$$\bar{M}_z = \frac{\sum\limits_{i=1}^{\infty} N_i M_i^3}{\sum\limits_{i=1}^{\infty} N_i M_i^2} = \frac{\sum\limits_{i=1}^{\infty} w_i M_i^2}{\sum\limits_{i=1}^{\infty} w_i M_i}$$

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

- 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 Mw/Mn ,called the *polydispersity index* or *PDI*.

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

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.

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

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 eq

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

$[\eta]$: 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 : $\eta_{rel} = \dfrac{\eta}{\eta_o} = \dfrac{t}{t_o}$

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

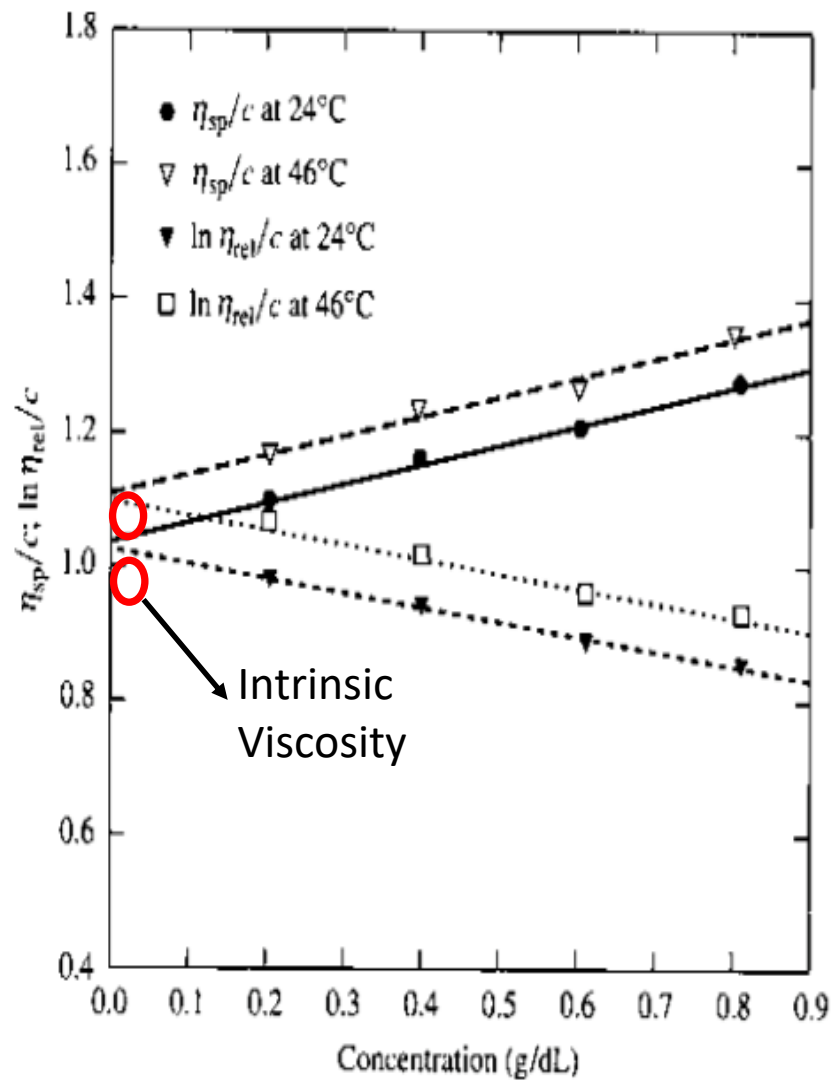$$\eta_{red} = \frac{t - t_0}{t_0 * c} = \frac{\eta_{sp}}{c}$$

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).

Example 1. *A polymer sample consists of 10% by weight of macromolecules of molecular weight 10,000 and 90% by weight of macromolecules with molecular weight 100,000. Calculate* $\overline{M}_n$ *and* $\overline{M}_w$.

Solution. As $\quad \overline{M}_n = \dfrac{\Sigma N_i M_i}{\Sigma N_i} = \dfrac{\Sigma W_i}{\Sigma N_i}$

where $\quad W_i$ = weight of ith constituent,

$\qquad N_i$ = number of moles of ith constituent,

and $\qquad M_i$ = molecular weight of ith constituent

Given $W_1 = 10$ gms. and $W_2 = 90$ gm.

$\therefore \quad \Sigma W_i = W_1 + W_2 = 10 + 90 = 100$ gm.

Since $\quad N_i = \dfrac{W_i}{M_i}$

Hence $\quad N_1 = \dfrac{10}{10,000} \quad$ and $\quad N_2 = \dfrac{90}{100,000}$

Now $\quad \overline{M}_n = \dfrac{\Sigma W_i}{\Sigma N_i} = \dfrac{W_1 + W_2}{N_1 + N_2} = \dfrac{10 + 90}{\dfrac{10}{10,000} + \dfrac{90}{100,000}} = 5.26 \times 10^4$

Similarly, $\quad \overline{M}_w = \dfrac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \dfrac{N_1 M_1^2 + N_2 M_2^2}{N_1 M_1 + N_2 M_2} = \dfrac{N_1 M_1{}^2 + N_2 M_2^2}{W_1 + W_2}$

$$= \dfrac{\dfrac{10}{10,000} \times (10,000)^2 + \dfrac{90}{100,000}(100,000)^2}{10 + 90}$$

$= 9.1 \times 10^4$

Example 2:

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:

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

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

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

Example 3. *In a polymer, there are 100 molecules of molecular weight 100, 200 molecules of molecular weight 1000 and 300 molecules of molecular weight 10,000. Find* $\overline{M}_n$, $\overline{M}_w$ *and PDI.*

Solution. $\overline{M}_n = \dfrac{\Sigma N_i M_i}{\Sigma N_i} = \dfrac{N_1 M_1 + N_2 M_2 + N_2 M_3}{N_1 + N_2 + N_3}$

$$= \frac{100 \times 100 + 200 \times 1000 + 300 \times 10{,}000}{100 + 200 + 300}$$

$$= \frac{3.21 \times 10^6}{600} = 5.35 \times 10^3$$

$\overline{M}_w = \dfrac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \dfrac{100 \times (100)^2 + 200 \times (1000)^2 + 300 \times (10{,}000)^2}{100 \times 100 + 200 \times 1000 + 300 \times 10{,}000}$

$$= 9.4 \times 10^3$$

$$\text{PDI} = \frac{\overline{M}_w}{\overline{M}_n} = 1.757$$

Example 4-

In a polymer sample, 30% molecules have a molecular mass 20,000, 40% have molecular mass 30,000 and rest have 60,000. Calculate mass average and number average molecular masses.

Solution

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{(30 \times 20,000) + (40 \times 30,000) + (30 \times 60,000)}{30 + 40 + 30}$$

$$= 36000$$

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{30(20,000)^2 + 40(30,000)^2 + 30(60,000)^2}{30 \times 20,000 + 40 \times 30,000 + 30 \times 60,000}$$
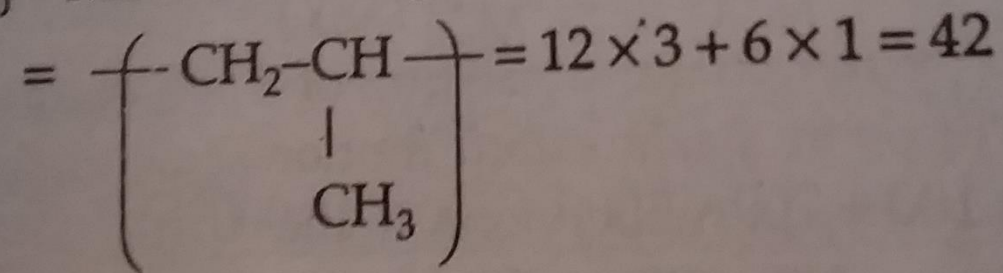
$$= 43333.$$

Example 6. Find $\overline{M}_w$ for PP given its degree of polymerization as 10,000.

Solution. Since $\overline{DP}_w = \dfrac{\overline{M}_w}{M_0}$

$$\therefore \quad \overline{M}_w = \overline{DP}_w \times M_0$$

where $\quad \overline{DP}_w = $ Degree of Polymerization = 10,000 (given)

And $\quad M_0 = $ Molecular weight of repeat unit of PP

$$= \left(\!\!-CH_2-CH-\!\!\underset{\underset{CH_3}{|}}{}\right) = 12 \times 3 + 6 \times 1 = 42$$

Hence, $\overline{M}_w = 10,000 \times 42$

$$\Rightarrow \quad \overline{M}_w = 42 \times 10^4 \text{ gm/mol}$$

Problem:

<u>Computations of Average Molecular Weights and Degree of Polymerization</u>

Assume that the molecular weight distributions shown in Figure 14.3 are for poly(vinyl chloride). For this material, compute:

(a) the number-average molecular weight,

(b) the degree of polymerization, and

(c) the weight-average molecular weight.

Molecular Weight Range (g/mol)	Mean M_i (g/mol)	x_i	x_iM_i
5,000–10,000	7,500	0.05	375
10,000–15,000	12,500	0.16	2000
15,000–20,000	17,500	0.22	3850
20,000–25,000	22,500	0.27	6075
25,000–30,000	27,500	0.20	5500
30,000–35,000	32,500	0.08	2600
35,000–40,000	37,500	0.02	750

$$\overline{M}_n = 21,150 \qquad \sum x_i M_i = 21,150$$

Where, x_i: Fraction of total no. of chain within the corresponding size change

$\overline{M}_n$: Number average molecular weight

Molecular Weight Range (g/mol)	Mean M_i (g/mol)	w_i	w_iM_i
5,000–10,000	7,500	0.02	150
10,000–15,000	12,500	0.10	1250
15,000–20,000	17,500	0.18	3150
20,000–25,000	22,500	0.29	6525
25,000–30,000	27,500	0.26	7150
30,000–35,000	32,500	0.13	4225
35,000–40,000	37,500	0.02	750

$$\overline{M_w} = 23{,}200 \qquad \sum x_i M_i = 23{,}200$$

Where, $\overline{M_w}$: weight average molecular weight

PVC: C_2H_3Cl

	C	H	Cl
Atomic weight (g/mol)	12.01	1.01	35.45

$\overline{m}=2(12.01)+3(1.01)+35.45$

$\overline{m}=62.50$g/mol

Number average degree of polymerization,

$$n_n = \frac{\overline{M_n}}{\overline{m}} = \frac{21,150}{62.50} = 338$$