▸ Sedimentation and viscosity average m.w : $\overline{M}_v$ & $\overline{M}_Z$

Apart from the $\overline{M}_n$ and $\overline{M}_w$, there are two other ways of expressing the M.W. based on the ~~to~~ sedimentation and flow behavior of the polymer in solution. They are: Z - average m.w ($\overline{M}_Z$) and viscosity average m.w ($\overline{M}_v$).

$$\overline{M}_Z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} \quad \text{and} \quad \overline{M}_v = \left(\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i} \right)^{1/a}$$

'a' is a variable (its value ranging from 0.5 to 1) in the Mark - equation, which relates viscosity (η) with $\overline{M}_v$.

▸ $\boxed{\text{N.B}}$: $\overline{M}_n$ and $\overline{M}_v$ can also be expressed as —

$$\overline{M}_n = \frac{\sum_{i=1}^{n} n_i M_i}{\sum_{i=1}^{n} n_i} \quad \text{or,} \quad \overline{M}_n = \frac{\int_0^M nM\,dM}{\int_0^M n\,dM}$$

$$\overline{M}_W = \frac{\sum_{i=1}^{n} n_i M_i^2}{\sum_{i=1}^{n} n_i M_i} \quad \text{or,} \quad \overline{M}_w = \frac{\int_0^M nM^2\,dM}{\int_0^M nM\,dM}$$

▸ $\boxed{\text{N.B}}$: The $\overline{M}_n$ is directly determined by membrane osmo . while the $\overline{M}_w$ is determided by light scattering or other scattering techniques. A measure of breadth of new distribution is given by the ratios of m.w averages. The most commonly used ratio is $\overline{M}_w/\overline{M}_n$, which is called polydispersity index or PDI.

▸ Molecular weight and Degree of Polymerisation :

If M is the M.W of a polymer, D_P is degree of polymerisation and m is the M.W of the monomer, then,

$$M = D_P \times m$$

Both D_P and M.W are related to the molecular size. Hence like the M.W, D_P can also be averaged over the size of the sample. The "number average" and "weight average" degree of polymerisation can then be defined in a manner similar to that of $\overline{M}_n$ and $\overline{M}_\omega$.

$$(\overline{D}_P)_n = \frac{\sum n_i (D_P)_i}{\sum n_i}$$

and,

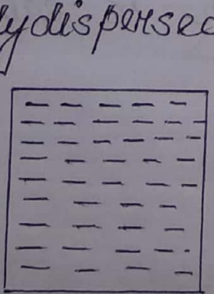
$$(\overline{D}_P)_\omega = \frac{\sum n_i (D_P)_i^2}{\sum n_i (D_P)_i}$$

Therefore, $\overline{M}_n = (\overline{D}_P)_n \cdot m$

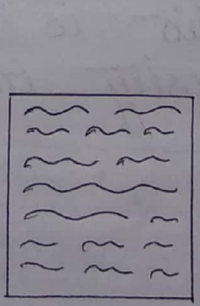
and $\overline{M}_\omega = (\overline{D}_P)_\omega \cdot m$

▸ Polydispersity and Molecular weight distribution:

When each of the molecules of a chemical compound has same molecular weight, it is called "monodispersed" system. In case of polymer, each of the polymer molecules can have different molecular weight, so it e is called 'polydispersed' system.



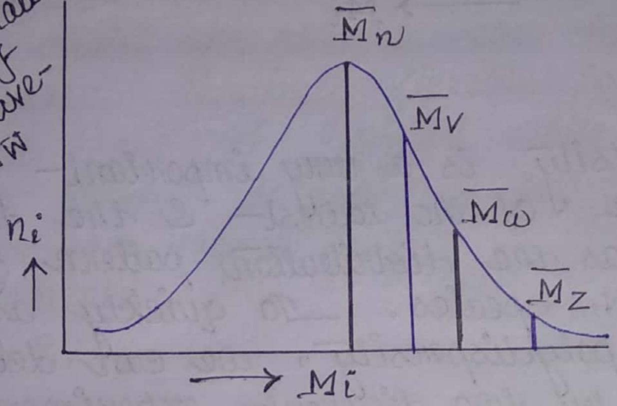
Monodispersed system



Polydispersed system

To know a polymer properly, we must have knowledge of both the average M.W as well as its dispersion pattern. This dispersity w.r.t. the lowest to the highest m.w homologues is expressed by a simple m.w distribution curve. Such a curve is obtained by plotting the number fraction (ni) of molecules having a particular m.w (M_i) against the corresponding m.w. The relative positions of various average m.ws in a polymer is shown below:

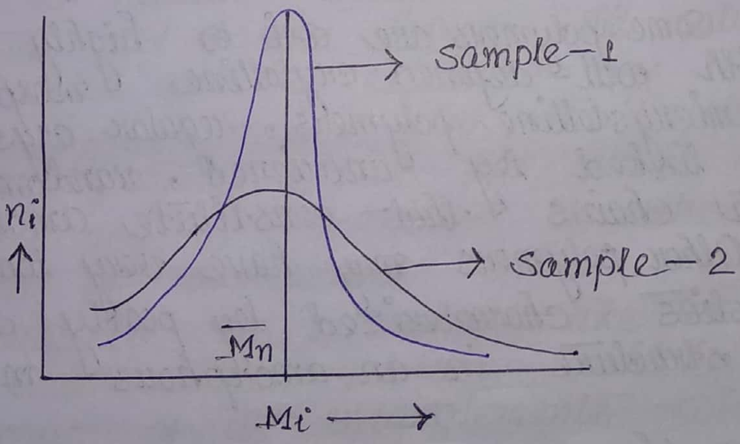
One sample showing relative position of various average M.W



A molecular weight distribution curve for a hypothetical polydispered polymer.

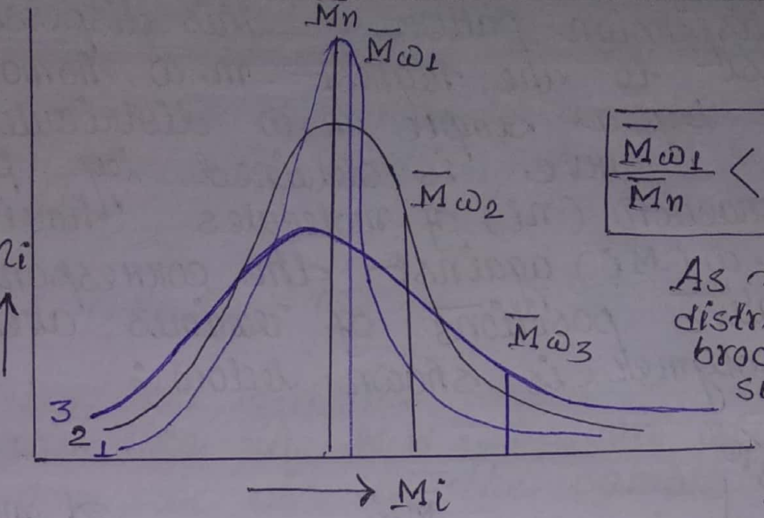
It may be noted that $\overline{M}_w$ is greater than $\overline{M}_n$ and that $\overline{M}_V$ is close to $\overline{M}_w$ ~~and~~ than to $\overline{M}_n$.

Two samples with the same $\overline{M}_n$, but different m.w distribution.



The above ~~s~~ figure shows M.w distribution in two samples having the same number average m.w but different polydispersities. Sample 1 obviously has a narrower dispersion pattern, hence, a lower polydispersity than the sample 2.

Three samples with the same $\overline{M}_n$ but different M.ω distribution



$$\boxed{\frac{\overline{M}_{\omega 1}}{\overline{M}_n} < \frac{\overline{M}_{\omega 2}}{\overline{M}_n} < \frac{\overline{M}_{\omega 3}}{\overline{M}_n}}$$

As the m.ω distribution becomes broder (i.e dispersity increases) the value of $\overline{M}_\omega / \overline{M}_n$ increases.

Polydispersity is a very important parameter. It gives an idea of the lowest & the highest M.ω. species as well as the distribution pattern of the intermidiate M.W. species. To quickly ascertain the degree of polydispersity, we can determine $\overline{M}_\omega$ and $\overline{M}_n$ by two different experimendal methods and then find the $\overline{M}_\omega / \overline{M}_n$. The ratio is indicative of the extent of polydispersity.

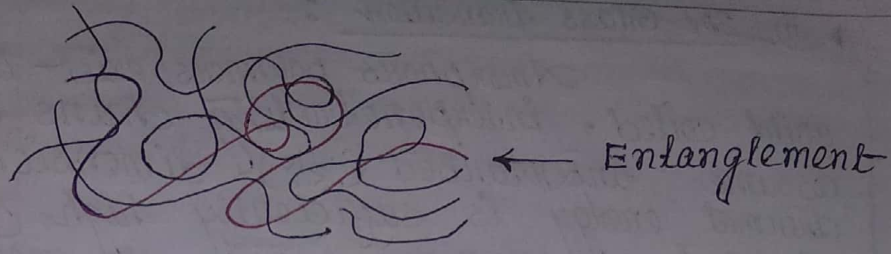
The solid state preparation of polymers

Some polymers are ~~all~~ ~~a~~ highly crystalline material with well defined crystalline morphology. In case of semicrystalline polymers, regular crystalline units are linked by unoriened, random conformation chains that constitute amorphous regions. Other polymers may have very low crystallinity ~~characteristics~~ characterized by poorly defined crystalline structure in an amorphous matrix.

(a) The amorphous state :

i) chain Entanglement and Reptation :

Polymers chains that are sufficienty long can form stable flow - restricting entanglements. Entanglements have significant importance in relation to viscoelastic properties, melt viscosity and mechanical properties.

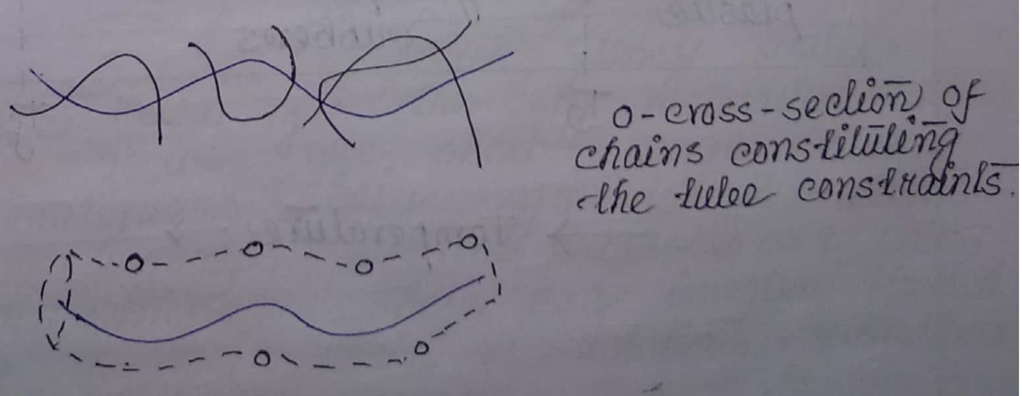


▶ Critical molecular weight :

The minimum polymer chain-length or critical molecular weight, M_c, for the formation of stable entanglements depends upon the flexibility of a polymer chain and also to the intramolecular steric hindrance. Relatively flexible polymer chains have a high M_c; A ~~related~~ while more rigid-chain polymers have a relatively low M_c. A related parameter is M_e, which is the M.W between entanglements. As a rough ~~re~~ rule of thumb, $M_c \approx 2M_e$.

▶ Reptation :

If individual chains are entangled in the solid state, the questions arises as to how long-range movement of chains can occurs as the polymer is heated through its glass-transition temperature and passes from the solid to the melt state. This can be explained by ~~the~~ theory developed by Gennes. In the melt state, individual polymer chains can move by local Brownian motion restricted by the topological constraint of neighboring chains. Movement can be visualized as snake-like motion (i.e reptation) of the chain within a tube, which is defined by the locus of its entanglements with neighboring molecules.



Reptation model