



ENGINEERING CHEMISTRY

Department of Science and Humanities



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Functional materials-Polymers



Class content:

- *Molecular weight of polymers*
 - *Number average molecular weight*
 - *Weight average molecular weight*
 - *Viscosity average molecular weight*

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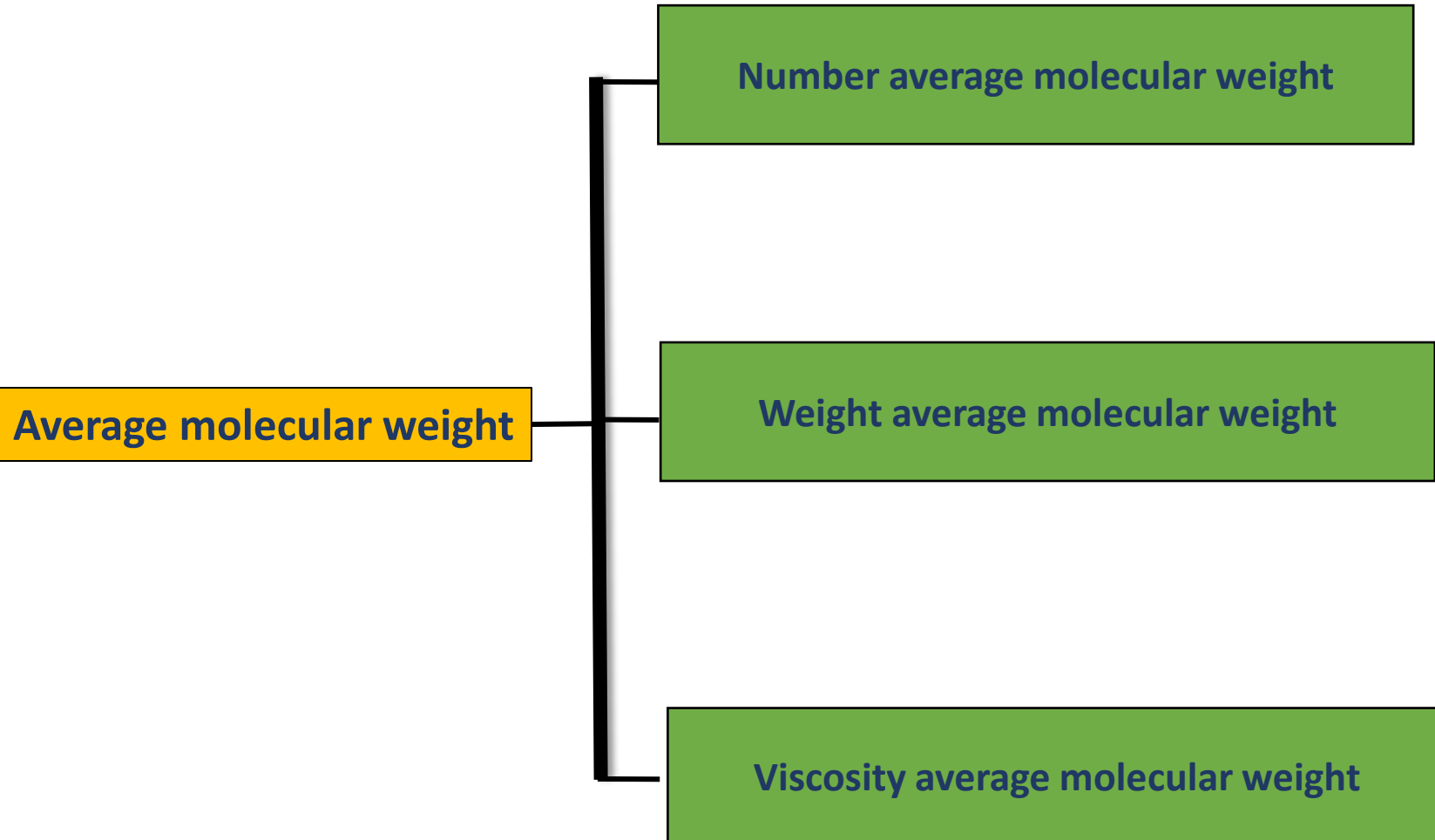


Molecular weight of Polymers

- Polymers are a **mix of chains of different lengths**
- Weight of polymers is expressed as an **average molecular weight**
- The molecular weight is an important characteristic of a polymer sample as **several properties of polymers** depend on the molecular weight
- The entire range of **mechanical properties** like stress-strain, impact, fracture, fatigue, creep, stress relaxation and cracking are influenced by average molecular weight and molecular weight distribution

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Number average molecular weight, \bar{M}_n

- Obtained by dividing the **total weight of the dispersed material** with the **total number of polymer units present**

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + \dots}{n_1 + n_2 + \dots}$$

where $n_1, n_2, n_3 \dots$ are number of polymer units having molecular weights $M_1, M_2, M_3 \dots$ respectively

$$\bar{M}_n = \sum n_i M_i / \sum n_i$$

where n_i is the number of polymer units of molecular mass M_i

- It depends only on **number of polymer units** and not their size
- Colligative properties** like osmotic pressure, elevation in boiling point or depression in melting point is used to determine number average molecular weight

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Weight average molecular weight, \bar{M}_w

- It gives representation to various molecular species in proportion to their **masses** in the given material
- In the averaging process, the molecular weight of each individual species is multiplied by its mass

$$\bar{M}_w = \frac{m_1 M_1 + m_2 M_2 + \dots}{m_1 + m_2 + \dots}$$

where $m_1, m_2, m_3 \dots$ are masses of polymer units having molecular weights M_1, M_2, M_3 respectively

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- if $n_1, n_2, n_3 \dots$ are number of polymer units having molecular weights M_1, M_2, M_3 respectively then $m_1 = n_1 M_1, m_2 = n_2 M_2 \dots$
- Weight average molecular weight can be written as

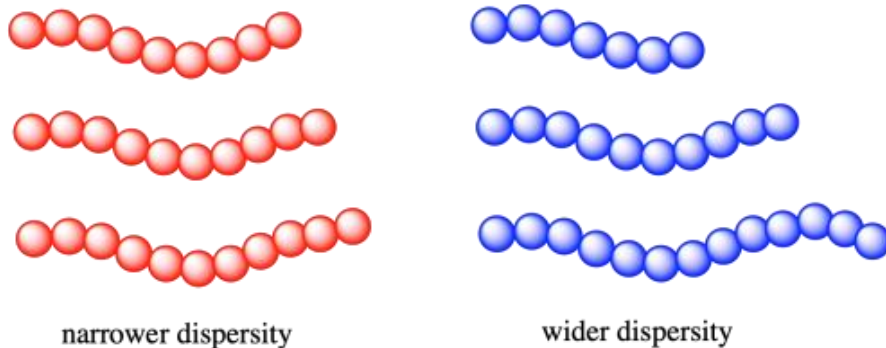
$$\begin{aligned}\bar{M}_w &= \frac{n_1 M_1^2 + n_2 M_2^2 + \dots}{n_1 M_1 + n_2 M_2 + \dots} \\ &= \sum n_i M_i^2 / \sum n_i M_i\end{aligned}$$

- It depends on **size** of the polymer units
- Properties which **depend on size** like sedimentation velocity or light scattering are used to determine weight average molecular weight

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- The ratio $\frac{\bar{M}_w}{\bar{M}_n}$ is called the **polydispersity index** (PDI)
- It is a measure for the broadness of a molecular weight distribution of a polymer, that is, the larger the polydispersity index, the broader the molecular weight distribution
- A monodisperse polymer where all the chain lengths are equal has PDI =1
- PDI > 1, shows that the polymeric sample is less homogeneous and polydisperse



Source: <http://employees.csbsju.edu/cschaller/Advanced/Polymers/CPmw.html>

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Viscosity average molecular weight, \overline{M}_v

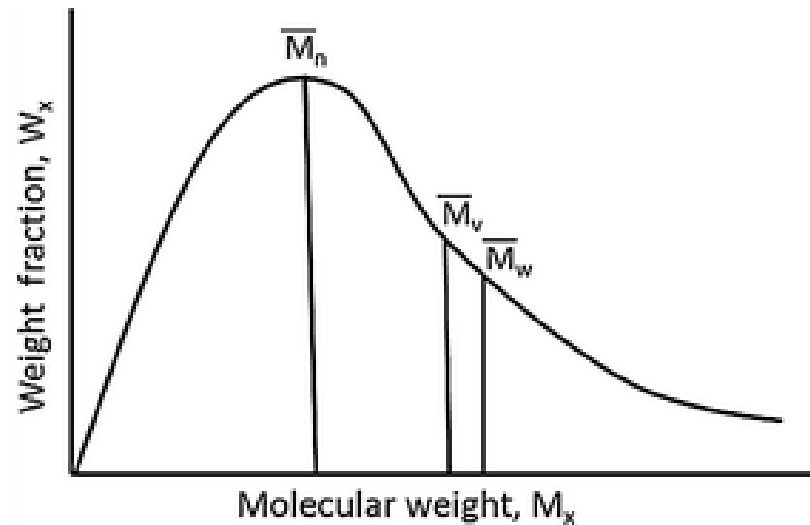
$$\overline{M}_v = \left[\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i} \right]^{1/a}$$

- **a** is the Mark- Houwink parameter
- its value depends on the **polymer- solvent system at a particular temperature** and is **$0.5 \leq a \leq 0.9$**
- Viscosity average molecular weight is closer to weight average molecular weight as **larger molecules contribute more to viscosity**

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Molecular weight distribution curve



Source: https://link.springer.com/chapter/10.1007/978-3-642-38730-2_2

$$\bar{M}_w > \bar{M}_v > \bar{M}_n$$



THANK YOU

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