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Molar Masses of Polymers

1. Definition of Polymers

A *polymer* is a high molar mass compound resulting from the concatenation of many *monomer* molecules by covalent bond formation. With the term *macromolecule* one refers to the individual molecule that constitutes a polymer material, while the term *polymer* is used interchangeably to describe macromolecules or the material resulting from them. **According to the International Union of Pure and Applied Chemistry (IUPAC), a macromolecule is "a molecule of relatively high molar mass, the structure of which essentially comprises the multiple repetition of units originating, actually or conceptually, from molecules of low molar mass, the monomers".** According to Hermann Staudinger, polymers are macromolecules for which chain length differences do not translate into physical property differences anymore, in contrast to small molecules, for which a change in the chemical structure usually goes along with a change in boiling point, melting point, polarity, etc. Such differences in properties can hence be exploited to separate small molecules, while macromolecular chains of different lengths are inseparable.

Polymers of different shapes can nowadays straightforwardly be synthesized. **The most common *polymer chain architecture* is that of *linear homopolymers*** that are composed of a linear concatenation of one single type of repeat unit. Such macromolecules can be made up of thousands of repeat units so that the *contour length* of the macromolecule (the length of the polymer chain) can exceed 1 μm.

Many of the useful mechanical properties that are uniquely associated with polymer materials (such as rubber elasticity, mechanical strength, toughness, viscosity) are a consequence of their high molar mass. However, contrary to a well-defined small molecule, polymers do not have a precise molar mass. Polymers are not *monodisperse* but *polydisperse*, that is, they are mixtures of molecules of the same repeat unit structure (in case of homopolymers) and chain architecture but different chain length and therefore different molar mass. In fact, most polymerization reactions produce "broad" molar mass distributions that are a function of the polymerization conditions and statistical processes involved in the underlying polymerization mechanism.

2. Properties of Distribution Functions

A distribution function can be characterized in terms of its different moments, which are quantitative measures describing the shape and spread of the distribution. In general, the k^{th} (raw) moment of a continuous distribution is defined as the expected value of its variable raised to the k^{th} power.

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$$\mu'_k = \int_{-\infty}^{\infty} x^k f(x)\, dx \ , \tag{1}$$

where $f(x)$ is the probability density function of the distribution that describes how probabilities are distributed over the possible values of the continuous random variable. By this definition, **the zeroth moment (k = 0) is equal to unity, while the first moment (k = 1) characterizes the mean of the distribution, μ.**

Higher moments are commonly expressed as **central moments**, which are defined about the mean μ (central moments are represented without the prime sign):

$$\mu_k = \int_{-\infty}^{\infty} (x-\mu)^k f(x)\, dx \ . \tag{2}$$

While the zeroth central moment ($\mu_0 = 1$) and the first central moment ($\mu_1 = 0$) do not provide much meaningful information about a distribution function, the second central moment is particularly important as it is equivalent to the variance, σ^2, which measures the spread (or the dispersion) of the distribution around the mean:

$$\sigma^2 = \mu_2 = \int_{-\infty}^{\infty} (x-\mu)^2 f(x)\, dx \ . \tag{3}$$

The standard deviation, σ, defined as the square root of the variance, is therefore directly related to the second central moment of the distribution. The standard deviation has the same units as the quantity that is being measured. Moreover, the third central moment (skewness) measures the asymmetry of the distribution, while the fourth central moment (kurtosis) characterizes the distribution of data points at the peak. For example, a higher kurtosis indicates more data points close to the mean and sharper peaks.

3. Molar Masses of Polymers

While it is possible to fully characterize the molar mass[1] distribution of a polymer, ϕ(M), using, for example, chromatographic techniques, it is generally more practical to characterize the molar mass distribution in terms of certain average molar masses that are linked to the moments of its distribution. However, molar mass distributions of polymers are discrete and not continuous. Therefore, the integral in Equation 1 must be replaced by a sum denotation:

$$\mu'_k = \sum_{x=1} n_x M_x^k \ . \tag{4}$$

[1] The term *molar mass* is defined as the mass of a mole of a particular substance and therefore expressed in g/mol. In contrast, the term *molecular weight* refers to the ratio of the mass of a molecule to the unit of mass (known as 'amu' or 'u', which is defined as 1/12 of the atomic mass unit of a C^{12} atom) and has no unit by definition. While the term *molecular weight* remains prevalent in the scientific literature in polymer science (and is often wrongly used with g/mol as the unit), its use has been deprecated in favor of *molar mass* by the IUPAC for many years.

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In case of a discrete distribution, nx does not necessarily need to represent a probability density function but can also represent a total number of counts or any other relevant weighting factor. For ϕ(M), nx may be the number of chains with a degree of polymerization x and the corresponding molar mass Mx.

The **number-average molar mass, $\bar{M}_n$,** is defined as the ratio of the first moment to the zeroth moment of the number-fraction distribution. $\bar{M}_n$ is hence equivalent to the sum of all molar masses of the chains present in the polymer, divided by the total number of chains. In other words, $\bar{M}_n$ is normalized against the total number of molecules, i. e., it is a weighted average based on the number of molecules or the **arithmetic mean of the molar mass distribution**

$$\bar{M}_n = \frac{\mu'_1}{\mu'_0} = \frac{\sum n_x M_x}{\sum n_x} = \frac{\sum n_x x M_0}{\sum n_x} = \frac{\sum w_x}{\sum n_x} \,, \tag{5}$$

where M_0 is the average mass of a repeating unit (equivalent to the molar mass of a monomer, when no leaving group is released during the polymerization) and w_x is the total mass of chains with degree of polymerization x.

$\bar{M}_n$ is relatively straightforwardly determined by different experimental techniques, and therefore often given on a commercial sample of a polymer. Depending on the context, however, $\bar{M}_n$ may not necessarily be very representative of the material because it overrepresents low molar mass chains. Therefore, the **weight-average molar mass, $\bar{M}_w$,** is often preferred, which is defined as the ratio of the second moment to the first moment of the number fraction distribution:

$$\bar{M}_w = \frac{\mu'_2}{\mu'_1} = \frac{\sum n_x M_x^2}{\sum n_x M_x} = \frac{\sum w_x M_x}{\sum w_x} \,. \tag{6}$$

The second raw moment in the numerator accounts for a more significant contribution of larger molar mass species in the mixture. As evident from Equation 6, **$\bar{M}_w$ is an average weighted for the total mass of all macromolecules in the distribution.**

In polymer science, the **width of a molar mass distribution is commonly described by the dispersity, *Đ*,**[2] which is defined as the ratio of $\bar{M}_w$ and $\bar{M}_n$. It can be demonstrated that *Đ* indeed provides a meaningful description of the width of the distribution as its definition based on the moments of the molar mass distribution allows to derive a relation to the standard deviation σ (see Appendix for the complete derivation):

$$Đ = \frac{\bar{M}_w}{\bar{M}_n} = \frac{\sum n_x M_x^2 \cdot \sum n_x}{(\sum n_x M_x)^2} = 1 + \frac{\sigma^2}{\bar{M}_n{}^2} \,. \tag{7}$$

The expression $\sigma/\bar{M}_n$ is also known as the relative standard deviation of the number distribution. Hence, for a materials sample where all species have exactly the same molar mass so that $\sigma = 0$, the dispersity is *Đ* = 1, for which reason such a sample is referred to as **monodisperse**. However, **all polymers are polydisperse so that *Đ* > 1**. Depending on the polymerization mechanism, the molar mass distribution

[2] In older literature and textbooks, the dispersity of a polymer material is also referred to as polymolecularity or polydispersity, and the corresponding parameter as polymolecularity or polydispersity index with the symbols *I* or *P* or *PDI*. But these expressions and symbols have long since been deprecated by the IUPAC in favor of the term and symbol dispersity *Đ*.

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may be referred to as "narrow", with $Đ \gtrsim 1$, where all the chains have roughly the same length (which is commonly but misleadingly referred to as "near monodisperse"), or "broad" where $Đ \gg 1$, and any increases in σ lead to disproportionately high increases in dispersity. In polymer science, the description of the molar mass distributions in terms of $Đ$ instead of σ became the norm because common experimental techniques typically give $\bar{M}_n$ and/or $\bar{M}_w$. It is also worth noting that, because $Đ \gg 1$ for many polymerization techniques, it is very important to pay attention whether a molar mass of a polymer sample is given as its $\bar{M}_n$ or its $\bar{M}_w$, which will differ by a factor of $Đ$.

4. Relevance of the High Molar Masses of Polymers

Many of the unique properties of polymers are due to their high molar masses. It is therefore essential to know about molar mass distributions, average molar masses, and dispersity as well as their dependence on the polymerization mechanisms.

- **Structural implications :**
  - Many polymer materials remain amorphous and vitrify at the glass transition temperature that is a function of the molar mass.
  - Polymers capable of crystallizing will do so only partially because chains become trapped in different crystals and entanglements, which results in semicrystalline polymers.
  - Polymers do not form a gaseous phase.
- **Processability :**
  - High viscosity in both solution and in the molten state allows for melt processing involving large deformations (film blowing, fiber drawing)
  - Viscoelastic behavior
- **Mechanical properties :**
  - Rubber elasticity
  - Plastic deformation
  - Polymer chain entanglement and mechanical resilience in tensile deformation

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Appendix

For the molar mass distribution of a polymer, the dispersity, Đ, is defined via the moments of the distribution (the limits of the sum ranging from 1 to the maximum degree of polymerization):

$$Đ = \frac{\bar{M}_w}{\bar{M}_n} = \frac{\sum n_x M_x^2 \cdot \sum n_x}{(\sum n_x M_x)^2} \ , \tag{8}$$

where x is the degree of polymerization. The standard deviation is defined as the root mean square difference from the mean. For calculating the variance, we replace the integral in Equation 3 with a sum due to the discontinuous nature of the molar mass distribution:

$$\sigma^2 = \sum (M_x - \mu)^2 n_x \ . \tag{9}$$

This expression reflects the total squared deviation from the mean. An expression for the variance analogous to the continuous case (Equation 3) requires normalizing this sum by the total number of chains. Such normalization is not necessary in Equation 3 as the integral already accounts for the density of the distribution, thus effectively weighting the squared deviations by the probability of each value occurring. This ensures that the variance accurately represents the average deviation from the mean.

$$\sigma^2 = \frac{\sum (M_x - \mu)^2 n_x}{\sum n_x} \ . \tag{10}$$

Expanding the sum of the numerator yields

$$\sigma^2 = \frac{\sum {M_x}^2 n_x - 2\mu \sum M_x n_x + \mu^2 \sum n_x}{\sum n_x} = \frac{\sum {M_x}^2 n_x}{\sum n_x} - 2\mu^2 + \mu^2 = \frac{\sum {M_x}^2 n_x}{\sum n_x} - \mu^2 \ . \tag{11}$$

Rearranging results in

$$\sum {M_x}^2 n_x = \sigma^2 \cdot \sum n_x + \mu^2 \cdot \sum n_x \ . \tag{12}$$

Substituting into the expression for Đ gives:

$$Đ = \frac{\bar{M}_w}{\bar{M}_n} = \frac{\sum n_x M_x^2 \cdot \sum n_x}{(\sum n_x M_x)^2} = \frac{(\sigma^2 \cdot \sum n_x + \mu^2 \cdot \sum n_x) \cdot \sum n_x}{(\sum n_x M_x)^2} = \frac{\sum n_x \cdot (\sigma^2 + \mu^2) \cdot \sum n_x}{(\sum n_x M_x)^2} \ . \tag{13}$$

From the definition of $\bar{M}_n$ in Equation 5 and recognizing that $\mu = \bar{M}_n$, it follows

$$Đ = \frac{\sum n_x \cdot (\sigma^2 + \mu^2) \cdot \sum n_x}{(\bar{M}_n \sum n_x)^2} = \frac{\sigma^2 + \mu^2}{{\bar{M}_n}^2} = 1 + \frac{\sigma^2}{\mu^2} \ . \tag{14}$$

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