



Tips & Tricks: GPC/SEC

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A look at the importance of molar mass average values.

Q: Why does a macromolecule have several molar masses and what do these indicate?

A: Macromolecules (with the exception of natural proteins and DNA) have a molar mass distribution (MMD). This means that even the simplest homopolymers consist of homologue chains with a different number of repeat units. Therefore, unlike low-molecular-weight components, macromolecules do not exhibit one definite molar mass. They are normally described with statistically based molar mass average values such as the molar mass averages of the number (M_n) or weight (M_w) and the polydispersity index (PDI).

Q: Why are these averages important?

A: M_n and M_w are calculated by averaging the number or the weight of polymer chains with a defined molar mass.

$$\bar{M}_n = \frac{\sum M_i \cdot n_i}{\sum n_i}$$

$$\bar{M}_w = \frac{\sum M_i \cdot w_i}{\sum w_i} = \frac{\sum M_i^2 \cdot n_i}{\sum M_i \cdot n_i}$$

$$\text{and PDI} = M_w/M_n$$

A simple example with a number of stones of different weight can help to understand the molar mass averages (Table 1).¹

M_n and M_w can be related to macroscopic properties of the macromolecules and are important parameters in, for example, the investigation of polymer kinetics. Additional information is available when the PDI is taken into account. Macromolecules can have similar M_w values but quite different M_n values. These differences in the average distribution values are indicated by the PDI value. However, the molar mass averages do not fully describe the macromolecule. This can only be done by the MMD.² Two samples can have the same molar mass averages M_n and M_w , but their properties can be different

because they have different MMDs. Molar mass averages can be determined from the MMD, but it is not possible to reconstruct the MMD from the averages alone.

Q: How broad is broad?

A: Figure 1 shows an overlay of the MMD for two different samples with nearly the same M_w . One of the samples has a MMD that is normally called "narrow" or "fairly narrow" because the PDI is below 1.1. The other sample has a higher PDI of around 2 and is normally addressed as a sample with a broad MMD. Figure 1 illustrates the range of the molar masses present in the samples. Even for the sample with the low PDI the molar mass range is from 58000–230000 Da. The sample with the broad MMD covers the molar mass range from 4000–800000 Da showing that samples with a relative low M_w of 124000 Da can

Figure 1: Comparison of a sample with a broad (blue) and a narrow (green) molar mass distribution with comparable M_w values.

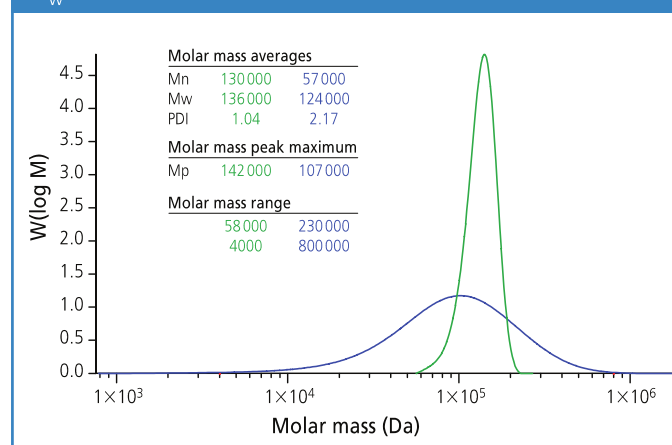


Table 1: Calculating M_w , M_n and PDI.

Composition of A

500 Stones with 1 kg = 500 kg
 2 Stones with 250 kg = 500 kg
 Total = 1000 kg

Composition of B

400 Stones with 1 kg = 400 kg
 100 Stones with 6 kg = 600 kg
 Total = 1000 kg

The number average molecular weight (M_n) for A and B is calculated by

$$M_n = \frac{\sum M_i \cdot n_i}{\sum n_i} = \frac{1 \cdot 500 + 250 \cdot 2}{500 + 2} = 1.99$$

$$M_n = \frac{\sum M_i \cdot n_i}{\sum n_i} = \frac{1 \cdot 400 + 6 \cdot 100}{400 + 100} = 2.00$$

The weight average molecular weight (M_w) for A and B is calculated by

$$M_w = \frac{\sum M_i \cdot w_i}{\sum w_i} = \frac{1 \cdot 500 + 250 \cdot 500}{500 + 500} = 125.5$$

$$M_w = \frac{\sum M_i \cdot w_i}{\sum w_i} = \frac{1 \cdot 400 + 6 \cdot 600}{400 + 600} = 4.00$$

The polydispersity index (PDI) for A and B is therefore

$$PDI = \frac{\bar{M}_w}{\bar{M}_n} = \frac{125.5}{1.99} = 63$$

$$PDI = \frac{\bar{M}_w}{\bar{M}_n} = \frac{4.00}{2.00} = 2.0$$

have very high-molecular-weight parts. It should also be noted that neither M_n , nor M_w can be assigned to the peak maximum of the eluting peak or the distribution. This distinct point is described with the molar mass at the peak maximum, M_p . M_p is a defined molar mass and not an average like M_n and M_w .

How are molar mass averages measured?

Several characterization methods are available to determine molar mass averages based on two principles: fractionating and non-fractionating. M_n or M_w (or both) can be measured, depending on which method is used. Table 2 describes the non-fractionating methods that can determine a single average.

There are only a few fractionating methods that allow the determination of the MMD and both averages:

- Gel permeation chromatography/size exclusion chromatography (GPC/SEC)
- Ultracentrifugation (UC)
- Field flow fractionation (FFF).

From these methods GPC/SEC is the most commonly used because it is easy-to-use and is also ideal for a wide range of molar masses, including higher molar masses and for broadly distributed samples.

What factors need to be taken into account to obtain reliable GPC/SEC measurements?

The molar masses for polymers are often underestimated. For samples with a low molar mass (approximately 124000 Da) and a broad MMD ($PD1 > 1.5$), fractions of several hundred thousand Da can be present.

GPC/SEC users should never underestimate the presence of high molar mass compounds in the sample. It is essential that the sample is given enough time to dissolve, which could be several hours. If the high molar mass fractions are not completely dissolved then the determined molar mass averages and PDI will be too low.

Table 2: Non-fractionating methods to determine molar mass averages (bulk properties).

M_n	M_w
Osmometry (membrane, vapour pressure)	Static light scattering (SLS)
Cryoscopy, Ebullioscopy	Dynamic light scattering (DLS)
End group analysis	Turbidimetry
Nuclear magnetic resonance (NMR) spectroscopy	Small angle X-ray scattering (SAXS)
Titration	Small angle neutron scattering (SANS)

High resolution columns covering a wide molar mass range are required to efficiently separate all the different molar mass fractions using GPC/SEC. A combination of several single porosity columns is often better than one single linear or mixed-bed column. Efficient separation is also required when intelligent detection like light scattering, viscometry, or triple detection is used. Insufficient separation (as a result of columns with low resolutions or exclusion limits) will allow the determination of a single molar mass average (e.g., M_w for light scattering) but never the determination of the other averages or the MMD.

It should also be noted that M_w and M_n are not related to a distinct point in the chromatogram or the MMD. They should not, therefore, be used to construct a GPC/SEC calibration curve. The best value to construct a calibration curve is M_p , the molar mass at the peak maximum. Please note that M_p is a

distinct molar mass and not a molar mass average. M_p can only be determined using GPC/SEC and should be on the certificate of every GPC/SEC molar mass calibration standard.

References

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