Polymer Molecular Weight Distribution and Definitions of MW Averages

Technical Overview

Introduction

Polymers consist of repeat units (monomers) chemically bonded into long chains. Understanding the physical properties of a polymer (such as mechanical strength, solubility and brittleness) requires knowledge of the length of the polymer chains. Chain length is often expressed in terms of the molecular weight of the polymer chain, related to the relative molecular mass of the monomers and the number of monomers connected in the chain. However, all synthetic polymers are polydisperse in that they contain polymer chains of unequal length, and so the molecular weight is not a single value - the polymer exists as a distribution of chain lengths and molecular weights. The molecular weight of a polymer must therefore be described as some average molecular weight calculated from the molecular weights of all the chains in the sample. This overview describes the commonly used molecular weight averages that can be determined by gel permeation chromatography (GPC) and size exclusion chromatography (SEC), how they are defined, and the classical methods originally used to measure them.

Number average molecular weight: Mn

The number average molecular weight is the statistical average molecular weight of all the polymer chains in the sample, and is defined by:

$$Mn = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

where M_i is the molecular weight of a chain and N_i is the number of chains of that molecular weight. Mn can be predicted by polymerization mechanisms and is measured by methods that determine the number of molecules in a sample of a given weight; for example, colligative methods such as end-group assay. If Mn is quoted for a molecular weight distribution, there are equal numbers of molecules on either side of Mn in the distribution.

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Weight average molecular weight: Mw

The weight average molecular weight is defined by:

$$Mw = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

Compared to Mn, Mw takes into account the molecular weight of a chain in determining contributions to the molecular weight average. The more massive the chain, the more the chain contributes to Mw. Mw is determined by methods that are sensitive to the molecular size rather than just their number, such as light scattering techniques. If Mw is quoted for a molecular weight distribution, there is an equal weight of molecules on either side of Mw in the distribution.

Higher average molecular weights: Mz, Mz+1

In general, a series of average molecular weights can be defined by the equation:

$$M = \frac{\Sigma N_i M^{n+1}}{\Sigma N_i M_i^n}$$

where: n = 1 gives M = Mw
n = 2 gives M = Mz
n = 3 gives M = Mz+1

The higher averages are increasingly more sensitive to high molecular weight polymers and accordingly are increasingly more difficult to measure with precision. They tend to be associated with methods that measure the motion of polymer molecules, such as diffusion or sedimentation techniques. Although the z-averages are not commonly quoted for polymers, several important methods for measuring the dimensions of chains that yield z-average molecular weights.

For all synthetic polydisperse polymers:

$Mn < Mw < Mz < Mz+1$

The polydispersity index is used as a measure of the broadness of a molecular weight distribution of a polymer, and is defined by:

$$\text{Polydispersity index} = \frac{Mw}{Mn}$$

The larger the polydispersity index, the broader the molecular weight. A monodisperse polymer where all the chain lengths are equal (such as a protein) has an Mw/Mn = 1. The best controlled synthetic polymers (narrow polymers used for calibrations) have Mw/Mn of 1.02 to 1.10. Step polymerization reactions typically yield values of Mw/Mn of around 2.0, whereas chain reactions yield Mw/Mn values between 1.5 and 20.

GPC/SEC-determined average molecular weights and Mp

SEC is the only technique that measures Mn, Mw, Mz and Mz+1 at the same time by measuring the entire distribution of the polymer. SEC also allows another average molecular weight to be calculated, the peak molecular weight Mp, defined as:

Mp = molecular weight of the highest peak

Therefore, Mp is the mode of the molecular weight distribution. Mp is quoted for very narrowly distributed polymers, such as polymer standards used in calibrations.

GPC/SEC columns and calibrants from Agilent

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Printed in the USA
April 30, 2015
5990-7890EN

Agilent Technologies