**Describing Polymer Molecular Weight: Mn, Mw, and Ð**

*Instructor Support Document*

*How to Use this Document*

This document accompanies a set of slides produced by the ACS MACRO initiative. It is meant to provide deeper explanation of the concepts and content found on these slides, supporting their use in the classroom. For each slide, we suggest how to walk students through the slide to promote learning, then we include background information that will assist you, the instructor, in teaching the material. This document is not intended for dissemination to students, but rather to bring you, the instructor, “up to speed” on this polymer content. You can choose what background information is relevant to your students and course, it is not necessary to include all background information in all teaching contexts. A glossary of new jargon is included at the start of this document, and a list of helpful references is included at the end.

*The Slides*

Slide 2 and 3: Offers practical examples to demonstrate why knowing molecular weight is important, both in terms of contrasting small molecule and polymer behavior and the effect of molecular weight on polymer properties

Slide 3: Introduces the illustrating example of the lesson. The chains are color-coded with their chain length.

Slide 4: Defines MN, the number-average molecular weight, its measurement, and its uses

Slide 5: Demonstrates how to calculate MN using the illustrating example

Slide 6: Defines MW, the weight-average molecular weight, its measurement, and its uses

Slide 7: Demonstrates how to calculate MW using the illustrating example

Slide 8: Defines Ð and describes how it is related to types of polymerization mechansims

Slide 9: Demonstrates how to calculate Ð using the illustrating example

*Glossary*

Backbone: The principal chain of a polymer, in which is defined the repeat unit

Chain-growth mechanism: A type of polymerization in which new monomers are added to an activated, propagating chain end; at any time during polymerization, the reaction mixture consists of rapidly growing chains and unreacted monomer

Condensation polymer: A polymer prepared by a chemical reaction between two functional groups, releasing a small molecule byproduct for each backbone bond formed.

Dispersity (*Ɖ*): The ratio of *M*w to *M*n for a polymer sample; an expression of the breadth of the molecular weight distribution in the sample

Endgroup: A functional group at the end of a polymer chain.

Living mechanism: A polymerization reaction with suppressed chain termination

Macromolecule: A large molecule consisting of linked repeating subunits; may also be a polymer

Molecular weight: The mass of a polymer chain, expressed in various units including g/mol

Number-average molecular weight (*M*n): The average molecular weight of polymer chains in the sample, weighted by number of chains that possess a given weight

Polymer: A large molecule consisting of covalently linked repeating subunits; created from monomers

Repeat unit: The simplest repeating structure in the polymer backbone

Step-growth mechanism: A polymerization mechanism in which polymerizable groups on any monomers or oligomers may react to grow the chain; unreacted monomer disappears very early in the polymerization and high molecular-weight polymer is only obtained after nearly full conversion

Vinyl polymer: A polymer derived from the polymerization of an alkene-containing monomer

Weight-average molecular weight (*M*n): The average molecular weight of polymer chains in the sample, weighted by the mass fraction of chains within the sample

Slide 2:

*Student walkthrough:*

Why do we need extra ways to measure and communicate polymer molecular weights? Consider the monomer, styrene, and its corresponding polymer, polystyrene. All molecules of styrene have a molecular formula of C8H8 and therefore a molecular weight of 104.15 g/mol. If we polymerize the styrene into polystyrene, however, we can make the chains as long or as short as we like. Further, not all of the chains in a given polystyrene sample have the same length. Take a look at the plot for an example of why this is important. As the length of a polymer chain increases, so does its Tg until it reaches a value plateau. If we wanted to make a plastic cup, we would need to make sure to use polystyrene that is long enough to have the right Tg, or our cups would be too soft to hold a beverage.

*Background:*

Synthetic polymers can take on a range of molecular weights dependent upon the type of chemical mechanism used to prepare them, the presence of impurities, or even the limitations of a manufacturing process. Many key material properties are somewhat-to-strongly dependent on polymer length. These include such things as:

* Tensile strength
* Impact strength
* Melt viscosity (longer chains entangle more, increasing viscosity)
* Percent crystallinity (shorter chains may not be able to crystallize)
* Crystallite size
* Solubility behavior (longer chains present a higher entropic cost to dissolve, so solubility decreases with increasing chain length)

For a given material, there is a threshold molecular weight above which the material has properties desirable for applications, but below which it is too short to be useful. Similarly, the increase in melt viscosity and decrease in solubility lead to a high molecular weight cutoff above which the polymer is too long to be feasibly processed. Therefore, knowing the average molecular weight of a polymer is a key factor in determining its suitability for a given application.

A further degree of complexity is added by the fact that there is a distribution of chain lengths within any particular polymer sample. This distribution may be made narrower or broader through choices in synthesis and processing. Narrower distributions may be desirable for creating nanoparticles, phase-segregated morphologies, or standard materials, but a broader distribution may also be useful. The longer chains can provide a degree of mechanical reinforcement and strength, while the presence of shorter chains can improve processability and add resilience or robustness. Therefore, having a measure of the breadth of the molecular weight distribution is also critical.

Slide 3:

*Student walkthrough:*

Many properties beyond Tg depend on polymer molar mass. Here are two more examples.

As the length of a polymer increases, so does its tensile strength. If we’re designing a polymer fiber for a rope, we want to make sure the individual chains are long enough to be strong enough. In general, increased chain length also leads to increased crystallinity and melt viscosity. In a sample that is a blend of chain lengths, we see a blend of properties as well. This can actually be useful for some applications.

We must also be mindful of using chains that are too long. The melt viscosity is how thick a polymer sample is when it is molten. We need to melt many polymers to process them into films, fibers, and molded products. If the melt viscosity is too high, it cannot be handled efficiently and may actually damage the processing equipment.

*Background:*

Consult the background material for slide 2.

Slide 4:

*Student walkthrough:*

We’ll use this box of cartoon polymers to learn about polymer molar mass. In this box, we have 1 two-monomer chain (dimer), 2 three-monomer chains (trimers), 3 four-monomer chains (tetramers), two five-monomer chains (pentamers), and 1 six-membered chain (hexamer). You can see that some chain lengths are more common, but others take up more space. These observations are what we try to quantify by calculating two different average molar masses.

*Background:*

This is a very simple example to help students understand the differences between MN, MW, and Ð, and how to calculate each value. You can substitute in molar masses of 1,000-6,000 for the chains if you wish to make the example seem more directly polymer-applicable. When you introduce the example it can be useful to ask the students how they would calculate the molar mass of the chains. Pointing out the most common chain length is 3. Is that sufficiently representative? Take a look at how much more of the space in the box is taken up by the three heaviest chains (the pentamers and hexamer) as compared to the lightest chains (the trimers and dimer).

Slide 5:

*Student walkthrough:*

Mn is the “number-average molecular weight”, and it is biased towards the most common molecular weight among the chains in the sample. The plot shows the distribution of chain lengths within a polymer sample as a function of the number of chains, Nx, and the molecular weight of those chains, Mx. Mn corresponds to the peak of the distribution, where the highest number of chains have a particular mass.

Mathematically, we divide the distribution curve into a number of slices to create pools of polymer chains of similar weight. The narrower these slices, the more precise our average will be. For each slice, we multiply the number of chains in the slice by the molecular weight of the slice and divide that by the total number of chains in the entire sample. We then add up the terms for all the slices to obtain the average. You can also think of this in terms of the mole fraction of each slice, Χx. Mn can be calculated by adding up the terms for the mole fraction of each slice multiplied by the molecular weight of the slice.

Size exclusion chromatography and MALDI mass spectrometry are very common methods for determining Mn. Each produces a distribution curve similar to the one seen in the plot above, the peak of which is generally Mn. But because Mn depends on the number of chains in the sample, we can also use various colligative property measurements to obtain Mn. Who can name a colligative property? Finally, we can also use end-group analysis to obtain Mn. This is any method that allows us to compare the number of end-groups in the sample to the number of repeat units in the sample. The ratio of end-groups to repeat units allows us to obtain Mn.

Knowing Mn is useful when we need to do stoichiometry, like calculating the amount of polymer needed to perform a post-functionalization reaction. It is also useful when we are discussing the thermodynamic properties of polymers, like their heat of polymerization.

*Background:*

Fractionating a polymer sample to obtain Mn can happen in a number of ways.

Size exclusion chromatography (SEC) fractionates the sample by hydrodynamic radius, or the size of the chain in solution. A dissolved sample of the polymer is passed through a column packed with finely porous beads. Smaller polymers get trapped in these pores, and therefore take longer to come off the column, while larger polymers stay in the eluent stream and come off the column quickly. Comparison of the retention time to standard curves permits a relative Mn to be obtained, to a near-infinite maximum value.

MALDI (Matrix-Assisted Light Desorption Ionization) mass spectrometry is a technique developed to facilitate the analysis of macromolecular samples. The polymer is embedded in a small molecule matrix, which absorbs light to ionize the polymer. Multiple ionizations occur, which permit the macromolecule to pass through the spectrometer for analysis. MALDI data look like an SEC curve made from individual molecular mass spikes. Each spike is a “slice” for analysis, weighted by the intensity of the peak. MALDI doesn’t require a standard curve and provides an absolute Mn to be obtained, but it typically only works well for macromolecules less than 107 g/mol in length.

Among colligative property methods, the most commonly used are viscometry and osmometry. Viscometry can be performed in either the solution or the melt, while osmometry necessarily requires a solution. Solution viscometry is a relative technique, in which the polymer solution viscosity is compared to that of a reference material and standard curve. Choice of solvent, choice of viscometer apparatus, and good temperature control are critical to obtaining dependable results. Melt viscometry removes concerns about solvent in exchange for a much higher viscosity to measure and the need to consider whether or not the sample is below its critical entanglement length. A different viscosity model must be applied if the sample is above or below that threshold. Osmometry works quite similarly to that for small molecules, but macromolecular samples take much more time to reach the static equilibrium needed for measurement. These measurements can take days or even months with polymer samples.

End-group analysis can be done with any method that can differentiate a chemical structure on the end of the polymer (for example from an initiator residue) from the repeat unit in a quantitative fashion. By far, this is most commonly done with nuclear magnetic resonance spectroscopy (NMR). In 1H NMR, the integration of a resonance on the end group is compared to the integration of a resonance in the repeat unit. The ratio of the two allows calculation of the average number of repeat units per chain. Multiplying that number by the mass of the repeat unit provides an absolute measure of Mn. This technique is fairly accessible, but sharply limited by the detection limits of the instrument. It is very difficult to obtain Mn values above approximately 20,000-30,000 g/mol by this method.

Slide 6:

*Student walkthrough:* In stoichiometry, anything we can say about molecules we can also say about moles. Therefore, let’s assume we have 1 mole of dimer, 2 moles of trimers, 3 moles of tetramers, 2 moles of pentamers, and 1 mole of hexamers. This way, we can set up terms multiplying the mass of each fraction by its mole fraction. Take note that the largest contribution to the average mass is that from the tetramers, the most common chain length.

*Background:*

While here we are using a simple mole fraction, in other methods we would actually use a kind of intensity fraction, or the portion of the total sample signal intensity represented by the “slice” of the sample in question.

Slide 7:

*Student walkthrough:*

Longer polymer chains have a larger effect on some important properties, so we also need to measure how much higher molecular weight material is in a sample. This information is provided by Mw, the weight-average molecular weight. This measurement is biased towards the heaviest chains that impact polymer properties.

To calculate Mw, you sum up the given term for each slice of the molecular weight distribution. It’s a more complex calculation than Mn because it is affording the longest chains more weight in the average. Another way to think about this calculation is that you’re adding up the weight fraction of a given slice, wx, multiplied by the molecular weight of that slice across all the slices in the distribution.

Mw can be measured by SEC and MALDI just like Mn, but Dynamic Light Scattering can also provide a measurement of this property. Depending on the type of DLS experiment, you can also obtain information about the shape of the polymer chain.

Mw is most useful for exploring material properties like Young’s modulus, tensile strength, bending strength, and more.

*Background:*

In a DLS experiment, polymer solutions are prepared at multiple, dilute concentrations. Dilute solution is used so that the Rayleigh scattering model can be used. Each solution is placed in the path of a laser beam, and the intensity of scattered light is measured at multiple angles off the beam path. Based upon the plot used to interpret the data, the Mw of the polymer can be obtained as well as information about the shape of the chain in solution and polymer-polymer and polymer-solvent interactions.

Key practical considerations in DLS experiments include the selection of the right solvent, as both the ability of the solvent to dissolve the polymer and the difference in refractive index between the solvent and polymer are important. Solutions also need to be entirely free from other particular contaminants like dust, so careful filtration of the sample solutions is required.

One particularly valuable application of light scattering in the determination of polymer molecular weight is the development of Multi-Angle Light Scattering detectors for SEC instruments. These detectors perform light scattering on the eluent as it leaves the column, allowing for an absolute measure of molecular weight.

Slide 8:

*Student walkthrough:* If we assume that each “bead” has a mass of 1 g/mol or 1 Da, then we have a total mass of 36 Da in the box. To calculate Mw, we are going to multiply the weight fraction of each chain length by the molar mass of that chain. For example, for our pentamers we need to multiply the 5 g/mol chain mass by 2 because there are two pentamer chains with a total mass of 10 Da. We divide the 10 by total sample mass of 36 Da to get the weight fraction, then multiply that by 5 Da once more to obtain the pentamer contribution to the Mw.

Notice that our Mw (4.333 Da) is higher than our MN (4.000 Da). This is expected because we are weighting the average towards the heavier chains.

*Background:* Relative measurements of Mw can be obtained by SEC, while absolute measurements can be obtained by DLS or MALDI-TOF.

Slide 5:

*Student walkthrough:*

The *dispersity* value was established to offer a simple and intuitive way to express the relative broadness or narrowness of the molecular weight distribution. It is calculated simply by dividing Mw by Mn. The larger this value, the greater the difference in chain lengths within your sample. We don’t measure Ð independently, rather we rely on measurements of Mn and Mw. If you are using SEC or MALDI for molecular weight analysis, you can easily obtain the values you need. If neither of these techniques is available to you, you’ll need to measure each weight by independent means.

High or low Ð values are not inherently “good” or “bad”, but they are useful for different applications. When Ð approaches closely to 1 (i.e. Ð < 1.05), we call that a “monodisperse” sample. When do you think monodispersity is important? Samples with Ð > 2 are called “polydisperse”. When might those be useful?

Further, particular methods of synthesizing polymers have expected Ð values. If you know a broad or narrow dispersity is your goal, then you should consider the polymerization methods that can most easily deliver those materials. Polymers made by condensation reactions end up with Ð of 2 because of how those reactions proceed. Chain growth mechanisms, commonly free radical polymerization, have middling Ð ranging from 1.3-1.6 depending on a number of factors. One of the characteristics of living polymerizations is a very low Ð. If your Ð is higher than predicted, this may indicate your polymerization has side reactions or there are impurities present.

In summary, any polymer sample should be characterized to obtain Mn, Mw, and Ð values so that scientists and engineers can identify the applications for which it is most suitable.

*Background:*

Ð is meant to be an easy way to express the breadth of the molecular weight distribution in a sample. Values between 1-2.5 are common. Values below 1 shouldn’t occur, simply based on the structure of the calculation.

The dispersity is important because it has powerful effects on material properties relevant to the processing and performance of polymer products. Understanding the effect of dispersity on these properties continues to be an area of intense interest. Much effort has also been expended upon developing synthetic methods that allow for the targeting of dispersity as well as average molecular weight.

Step-growth polymerizations possess theoretical dispersity values of 2. This is because the geometric molecular weight growth of these mechanisms results, on average, of a polymer chain doubling in size every time a new backbone bond is formed. These mechanisms include the polycondensation reactions that make commodity polyamides, polyesters, and polycarbonates, as well as more exotic reactions like Acyclic Diene Metathesis (ADMET).

Chain-growth polymerizations possess narrower Ð than step-growth, for reasons related to their mechanisms. In these reactions, an initiator starts a polymer chain by reacting with a monomer and generating an active site. That active site is the only place new monomers can add to the chain. Radicals are very common active sites, as are cations and anions. Radical and cationic polymerizations are vulnerable to side reactions and terminations that can broaden the weight distribution. This includes early termination or chain transfer that leads to shorter chains, and bimolecular coupling that leads to longer chains. SEC or MALDI data can often be diagnostic of the particular issue.

Living polymerizations are partially defined by their narrow dispersity. Monodispersity, Ð < 1.05, is readily achievable by taking care with choice of monomer and reaction conditions. These polymerizations achieve such control of dispersity and molecular weight through several characteristics:

* Fast, quantitative initiation
* Suppressed irreversible termination
* Conserved end-groups

In short, all chains start at the same time, grow and the same rate, and do not irreversibly die. There are a wide variety of polymerizations classified as living. Anionic polymerization is living provided the system is sufficiently dry and free of opportunities for side reactions and termination. Several methods for radical-based reversible activation-deactivation polymerization exist, most prominently Nitroxide-Mediated Polymerization (NMP), Atom Transfer Radical Polymerization (ATRP), and Reversible Addition-Fragmentation Chain-Transfer Polymerization (RAFT). Finally, many ring-opening polymerizations qualify as living. Ring-Opening Polymerization of lactams or lactides provides access to monodisperse polyamides and polyesters unavailable by step-growth methods, and Ring-Opening Metathesis Polymerization (ROMP) produces well-controlled polyolefins.

***Useful References***

*Websites*

ACS Division of Polymer Chemistry (POLY) - <http://www.polyacs.org/Home>

Their education section contains a large number of resources at all education levels.

ACS Division of Polymer Materials: Science and Engineering - [https://pmsedivision.org/#](https://pmsedivision.org/)

The “Teaching Polymers” section (under “Resources”) provides a more multidisciplinary set of resources for polymer education.

LearnChemistry from the Royal Society of Chemistry - <http://www.rsc.org/Learn-Chemistry>

Find a number of premade teaching modules for various settings (lab, lecture, etc.) and education levels (K-12, secondary).

A Brief Introduction to Polymer Nomenclature (IUPAC) - <http://iupac.org/publications/pac/pdf/2012/pdf/8410x2167.pdf>

*Books*

Introduction to Polymer Chemistry by Charles E. Carraher, Jr. Currently in the 4th edition from CRC press.

Contemporary Polymer Chemistry by Harry R. Allcock, Frederick W. Lampe, and James E. Mark.

Principles of Polymerization (4th ed.) by George Odian