# Molecular mass determination of polymers by fractional precipitation

Literature: P.W. Atkins: *Physical Chemistry*, Chapter 17D (Macromolecules and self-assembly–Determination of size and shape; X. ed.).
Type of practice: Individual.
Aim of the practice: To characterize the molecular mass distribution of epoxy resin samples by the methodology of fractional precipitation.

## 1    Introduction

### 1.1    Characteristics of molecular mass distribution functions

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 relative molecular mass (M) of the polymer chain, which is related to the relative molecular mass of the monomers and the number of monomers connected in the chain. However, all synthetic polymers are polydisperse, which is the result of multi-step reactions occurring simultaneously in a reaction mixture during the formation of a polymeric product (bulk solid polymer or polymer solution). Polydispersity means that the investigated sample contains polymer chains of unequal length, and so the molecular mass is not a single value – the polymer exists as a distribution of chain lengths and molecular mass. Even in a highly diluted polymer solution of a small volume, the number of the dissolved macromolecules falls in the range of billions[1]. The degree of polymerization (the number of linked monomers) cannot differ by many orders of magnitude even in a real, macroscopic polymer sample, we can be sure that even a polydisperse sample is a mixture, which contains many millions of polymer molecules, the mass (and chain length) of which is just identical. This set (population) of molecules of identical mass is called as a *fraction*. The summation of these fractions provide the total mass (or total amount) of macromolecular solutes in a sample.

The synthesized polymer can be polydisperse, that is, can contain highly different molecules, or can be fairly monodisperse, when a fraction of a characteristic molecular mass is present in the sample in a large relative amount. A polymerization process may also lead to a product in which a few different populations are present in a large amount. This system is termed as paucidisperse.

The molecular mass of a polymer is described as an *average molecular mass* calculated from the molecular mass of all the chains in the sample. The average molecular mass are generally less informative on the true composition of the polydisperse system. While the breadth of the distribution can be characterized by a numerical value (dispersity, Đ)[2], this cannot supplement fully the determination of the more informative representations, which are the so-called distribution functions. Two of such functions are in use: (1) the *differential* distribution function (DDF) and (2) the *cumulative* (also known as: integral) distribution function (CDF). The DDF provides the ratios which represent how large are the relative fractions that fall into the respective molecular mass intervals. The integral of the DDF is the CDF, which shows us the total mass of the molecules in the sample which are smaller than the respective mass value.

The molecular mass distribution of polymer samples is influenced by the kinetic aspects of the reaction steps (e.g., the chain growth), the type of polymerization and the technological process (e.g., bulk or suspension polymerization), but in the case of equilibrium reactions, even the way how the side products[3] (if any) are separated. The ideal, step-like polycondensation affords low-dispersity ((Đ = 2) polymer products,

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[1]This magnitude is well illustrated by the number of dissolved, 100.000 Da macromolecules in a 1 $\mu$L solution of 1 ppm (mg/L) concentration, which equals to 6 billions. This is not much less than the current human population of the Earth! Note: Da is a unit of molecular mass: a unit dalton is approximately numerically equal to the molar mass of the same expressed in g/mol (1 Da $\approx$ 1 g/mol).

[2]The dispersity of the sample (formerly known as: polydispersity index) is defined as the ratio of the mass-averaged and the number-averaged molecular masses, and is proportional to the breadth of the distribution curve.

[3]For polycondensation reations, side products are most often water or hydrochloric acid.

while the typical addition polymerization reactions produce samples of higher (between 5 to 20) dispersity. It is very important to know the molecular mass distribution of polymers because it heavily influences the physicochemical properties (mechanical, rheological properties, durability and wear properties, or even their resistance against water or other solvents) of the related plastic products.

## 1.2 Precipitation-induced fractionation (fractional precipitation)

The molecular mass distribution of a polymer sample can be determined if we fractionate the mixture and determine the amount of molecular mass of each fraction separately. This is possible by some modern instrumental analytical methods. Two main methods are widely utilized for fractionation: the matrix-assisted laser desorption ionization time-of-flight *mass spectrometry* (MALDI-TOF-MS) and *gel permeation chromatography* (GPC). These techniques, though, are scarcely available in an average laboratory owing to their high price and maintenance costs.

*A more widely available method* for the molecular mass distribution characterization is *the fractional precipitation*. This method is theoretically the same for small and large molecules: by addition of another solvent (precipitant) to a solution, in which the solute does not dissolve, the molecules of the solute will gradually precipitate. The increasing amounts of the precipitant will induce the separation of crystalline solids (for small molecules) and concentrated solutions (coacervates) or loose, floc-like precipitates (floccules) in the case of macromolecules. In practical terms, we prepare a dilute solution from the polymer to be fractionated and add the precipitant in a drop-by-drop fashion during intense stirring. The separation of the fraction with the largest molecular mass is indicated by the turbidity of the liquid. The gel phase can then be separated from the liquid solution. After the removal of the first fraction, we add a certain volume of precipitant to the remaining polymer solution so that the second fraction is also phase-separated, and then by a consecutive addition of precipitant volumes a series of polymer fractions are removed. Now, these fractions can be treated separately: they are redissolved in a good (well solvating) solvent and their average molecular masses are determined. This last step, however, takes long time and much effort – therefore, a fast methodology has been elaborated, which does not separate the individual polymer fractions, but considers the cumulative contributions of fractions and the molecular mass of each fraction is calculated from the actual concentration of the precipitant. This can be experimentally performed by the gradual addition of the precipitant to the macromolecular solution and monitoring the the turbidity change[4]. The mass fraction, (which is the ratio of the mass of the precipitated polymer and the total mass of polymer that was originally dissolved), can be determined as

$$m_r = \frac{\tau_v \times (V_0 + v)}{(\tau \times (V_0 + v))_{max}}$$

where $V_0$ is the volume of the initial polymer solution, $v$ is the volume of the precipitant, $\tau_v$ is the turbidity measured at the volume $v$, $(\tau \times (V_0 + v))_{max}$ is the maximum (turbidity × total volume) value. This empirical equation is based on the observation that in this system the turbidity of the system is proportional to the precipitated mass of the polymer (taking into account the degree of dilution).

The M relative molecular mass (that corresponds to a certain precipitant concentration) can be calculated by the Schulz equation:

$$M = \frac{B}{100\,\varphi - A}$$

where A and B are constants characteristic for the solvent–polymer–precipitant system and $\varphi$ is the volume fraction of the precipitant. The preliminary calculation of these constants by modeling the solvation conditions is very difficult and less reliable. Thus, these need to be determined experimentally by separating the polydisperse system to fractions and determining their average molecular mass by invoking an absolute method for the molecular mass determination (for example, ultracentrifugation, osmometry or light scattering). Then, by using the A and B constants, it is possible to use the above fast method in a practical sense.

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[4]Turbidity is the apparent absorbance of the incident radiation due to scattering.
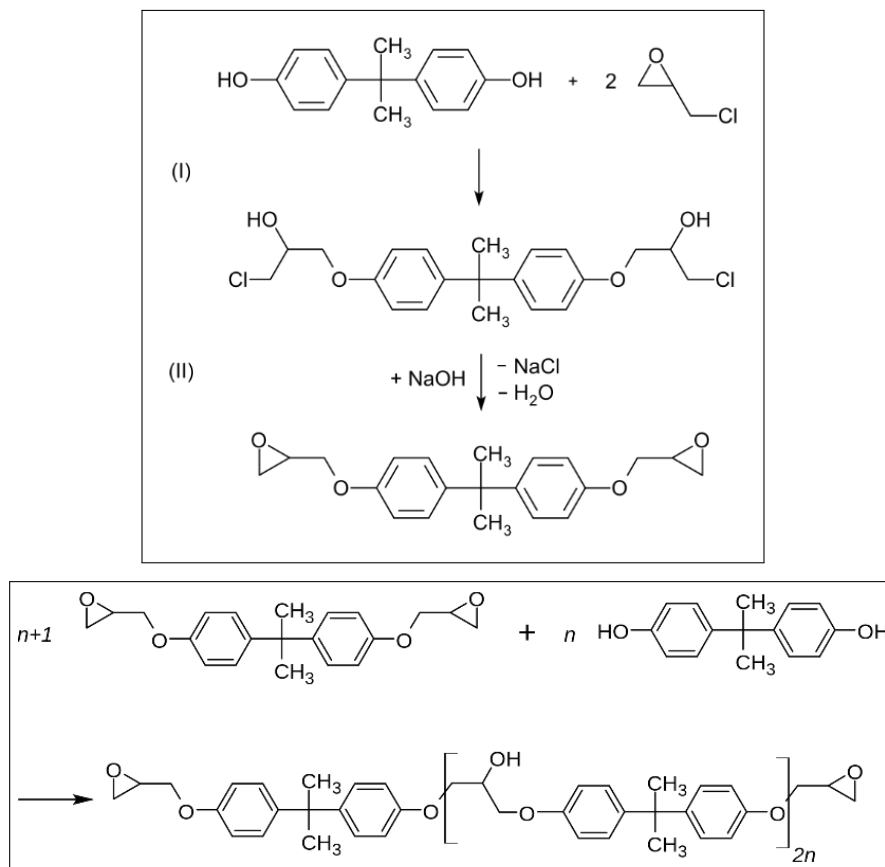
Figure 1: **Top**: Formation of bisphenol A-diglycidyl ether (*Badge*). **Bottom**: Second step of epoxy pre-polymer formation. One of the reactants (here epichlorohydrin) is applied in small excess to ensure the consumption of *bisphenol A* during polymerization, thus only epoxy group stays at the end of the chains. Therefore, no further polymerization is possible after the synthesis and the sample will not be subjected to long-lasting molecular mass change.

## 1.3  Preparation and characterization of epoxy resins

Highly crosslinked network polymers (duromers) are often prepared from epoxy resins. Their abundance is attributed to their flexible applicability and excellent properties. Combining them with crosslinkers, the (originally linear) polymer's epoxy group opens and binds to the other molecules, forming a network structure. The formed product bears excellent mechanical and electric properties and can be used as a polymeric matrix material in polymer composites. The chemical basis of the two-component, fast hardening glue is also the fast crosslinking process that takes place after mixing the linear-chain base resin with the crosslinker (e.g., polyamines).

The epoxy resin can be prepared in several ways. In one method, diphenilolpropane (*diane* a.k.a. bisphenol A) is reacted with epichlorohydrin in a strongly alkaline (NaOH) medium according to the reaction schemes found in Figure 1. Bringing the reaction forth we can create linear polymer chains, in which the polymerization degree (the number of monomeric units) is typically between 2 and 25[5].

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[5]In principle, reacting equimolar amounts of monomers, the degree of polymerization depends on the conversion and tends towards infinity (see the equations named after the inventor of nylon, W.H. Carothers, in the literature of the step polycondensation). However, under practical conditions, the reaction results in only ca. $20-30$ polymerization degrees. A very high conversion ($> 99\%$) is required to synthesize a structural materials consisting of a truly polymer like material after the linkage of several hundreds of monomers.

# 2 Description of the experimental procedure

We determine the molecular mass distribution of an epoxy resin solution by its turbidimetry-assisted fractional precipitation.

## 2.1 Measurements

Using the available graduated glass volumetric cylinders, you should prepare a 60 mL mixture of 80 v/v% dioxane and 20 v/v% acetone (unless it is already available under the hood or on your bench). Using this mixture as a binary solvent, prepare epoxy resin solutions in 0.75 g/L mass concentration in a 50 mL volumetric flask from all types of resins that you received in solid powder form. In order to accelerate the dissolution process, the resin may need to be pulverized in a mortar before making the solution. We suggest to ask the instructor about this. If the solution happens to retain a clearly visible cloudiness even few minutes after the complete dissolution (which indicates that the resin was not dehydrated properly), we advise that you ask or choose another sample for investigation.

Next, introduce 15 mL of epoxy resin solution by a graduated pipette into the available 100 mL screw-capped glass bottle (usually it is a blue-capped *Duran bottle*). The cap has a hole in the middle, which serves for the introduction of the precipitant (here water) and also serves for taking samples for turbidity measurements. Insert a magnetic bar into the bottle, and use stirring for the whole duration of the experiment.

Plan the experiments beforehand by calculating the necessary precipitant volumes for the successive precipitation of the polymer fractions from the solution. For this, calculate the relative molar mass of the possible polymeric species when the polymerization degree is between 25 and 2, using the relative molar mass of the repeating unit and the prepolymer. According to the Schulz equation, calculate also the volume fraction ($\varphi$) which is needed for the precipitation of the subsequent polymer fractions. Finally, also calculate the volume of water ($\nu$) which is needed to be added to the 15 mL initial solution, in order to reach the corresponding volume fraction. Fill Table 1 based on the above calculations! For the present polymer–solvent system, the parameters of the Schultz equation are $A = 7.3$ and $B = 1.64 \times 10^5$.

Table 1: Summary of experimental results.

| Measurement | Degree of polymerization | M | $\varphi$ | $\nu$ (mL) |
|:-----------:|:------------------------:|:-:|:---------:|:----------:|
| 1 | 25 | | | |

Before starting the measurements, you need to scrutinize the user manual of the turbidimeter (Hanna 98703), which is attached to this description or found separately at your workplace. Then, calibrate the instrument by using all four calibration standard samples, the nephelometric turbidity unit (NTU) of which are 0.1; 15; 100 and 750. Make sure you do not open the standard samples in the sealed vials!

Based on the calculated precipitant volumes, you can start adding water slowly, dropwise, to the epoxy resin solution from the burette, during continuous stirring. You can use an automatic pipette as well, if it is available. After the addition of each liquid precipitant portion, wait two minutes before pouring the sample volume into the glass vial that fits to the sample holder of the instrument. The minimum volume is 10 mL, as indicated by the line at the side of the vial. The liquid sample should also be stirred during the measurement, so you should add a small magnetic rod also into the vial, and place the whole turbidimeter over the magnetic stirrer plate. After reading the actual NTU values, the liquid content of the vial should be quantitatively transferred back to the Duran glass bottle, and then the fractionation is continued by adding the next portion of water sample, mixing and reading NTU, and then repeating the whole procedure based on the preliminary plan.

## 2.2 Evaluation of results

Based on the experimentally obtained data, complete Table 2 with numerical values.

Table 2: Summary of experimental results.

| Measurement | v (mL) | $\varphi$ | $\tau_v$ (NTU) | M | $m_r$ | Deriv. |
|---|---|---|---|---|---|---|
| 1 | | | | | | |

- For the calculation of $m_r$, find the maximum value of $\tau \times (V_0 + v)$ and the other $\tau \times (V_0 + v)$ values. This data point might not be the last one (corresponding to the largest volume of water). If so, you should omit all the data points after this maximum from further consideration and you do not need to calculate or tabulate any other data after it.

- Plot $m_r$ as a function of M, and also (1-$m_r$) as a function of M, separately in two different figures. Indicate in your report, which function is the CDF and which one is its mirror image.

- Derive CDF graphically (or by a computer software if the teacher requests so) and plot the as-obtained differential molecular mass distribution function as well. In Table 2, indicate the derivative values in case they were calculated by the respective molecular masses and not e.g., by arbitrary points of a hand-made contour curve of the CDF. In the column *Deriv*, indicate whether the derivatives are tabulated based on the $m_r$ *vs.* M or based on the (1-$m_r$) *vs.* M function.

## Questions

1. Why is it important to know the molecular mass distribution of a polymer sample?

2. Which factors influence the molecular mass distribution of polymer samples?

3. What is the differential distribution function?

4. What is the integral distribution function?

5. What do the terms (a) monodisperse, (b) polydisperse and (c) paucidisperse mean?

6. What is the meaning of turbidity? How can it be used to determine the relative mass of precipitated polymer?

7. What is an epoxy resin and how can it be synthesized? Do not provide detailed reaction steps, but simply indicate the names of typical reactants and the type of reaction and $1-2$ characteristics of the reaction.

8. If the relative mass of a polymer fraction is expected to be 3750, how large volume is the water that needs to be added to precipitate $15\,\text{mL}$ of polymer solution? The parameters of the Schulz equation are $A = 7.3$ and $B = 1.64 \times 10^5$.