Characterization of the molecular mass distribution of polymers by fractional precipitation

Theoretical background: Atkins: Physical Chemistry, Chapters 26.1–3
Type of the practice: Individual.
Aim of the practice: To determine the molecular mass distribution of epoxy resin samples by fractional precipitation method.

1. Introduction

1.1. Interpretation of molecular mass distribution

In most polymer solutions, the size of the statistical skein (or the length of the polymer chain) is different, which is mainly due to the sometimes very complex, multi-step (consisting of many elementary reactions running in parallel) formation mechanism of macromolecules.

Even in a very small volume and very dilute polymer solution, the number of dissolved macromolecules is in the order of at least billions. Since the degree of polymerization (number of monomers bound) cannot vary orders of magnitude in a realistic sample, we can be sure that a polydisperse sample containing a mixture of a very wide range of molecules of different polymerization, will contain many millions of molecules of exactly the same mass (same chain length). The set (population) of these molecules of the same mass is called the fraction. The total amount of solute in the sample is derived from the total amount of substance of each fraction, and /or of the total mass.

The polymer produced can be polydisperse, i.e., it can contain components of various molecular mass, and can be nearly monodisperse when a large percentage of a given molecular mass fraction is present. During the polymerization, a product can be formed in which several molecular masses are present in particularly high percentages. Such a system is called a paucidisperse.

The so-called average molecular mass alone provides very little information about the actual state of the polydisperse system. Although a numerical value (dispersity) can be used to characterize the width of the distribution, it cannot completely replace the determination of the more informative frequency functions. The most frequently used frequency functions are the relative frequency function (differential distribution function) and the sum curve (integral distribution function). The relative frequency function determines what proportion of the total mass of the polymer falls in each molecular mass range. This is integrated to the sum curve, which shows the total mass of molecules in the sample with a mass lower than the given molecular mass (the sum of the mass fractions of the corresponding fractions).

1.2. Fractional precipitation (fractional separation)

The molecular mass distribution of a given polymer sample can only be ascertained by fractionating the mixture and determining the amount and molecular mass of each fraction separately. This is possible with modern instrumental analytical methods. However, due to their cost requirements, these methods are rarely available in routine laboratory practice.

A more widely feasible method for determining the molecular mass distribution is fractional precipitation. This process is basically the same for macromolecular and small molecule compounds: if another solvent in which the solute is insoluble (precipitant) is added to a solution of a substance, the solute gradually precipitates. The addition of a precipitant usually results in the formation of crystals in the case of small-molecule compounds and in the case of polymers, usually in the form of a concentrated solution (coacervate) or a looser, often flocculent precipitate.

In practice, a dilute solution is prepared from the polymer to be fractionated and the precipitant is added dropwise with vigorous stirring. Separation of the highest molecular mass fraction is indicated by the turbidity of the solution. The gel phase is separated from the solution phase by decantation. After the first

fraction has been separated, enough precipitant is added to the remaining solution to separate the second fraction, and a series of fractions can be recovered from the solution by adding further precipitant. Redissolving each fraction in a well-solvating solvent we can determine their molecular masses.
However, this work takes a long time, so a fast method has been developed to determine the molecular mass distribution, which does not separate the individual polymer fractions, but summarizes the amount of fractions formed during continuous precipitation and determines the molecular mass from the precipitant concentration. One way to do this is to gradually add the precipitant to the dilute polymer solution and measure the change in turbidity of the polymer solution. The mass fraction as a measure of the relative amount of precipitated polymer (the ratio of the mass of the precipitated polymer to the total mass of the polymer originally dissolved) can also be determined for epoxy resins and other polymers to be tested in practice, such as

$$m_r = \frac{\tau_v \cdot (a+v)}{(\tau \cdot (a+v))_{max}}$$

where a is the volume of the starting polymer solution, v is the volume of precipitant added, τ_v is the turbidity measured at volume v, $(\tau \cdot (a + v))_{max}$ is the maximum value of (turbidity × total volume). This empirical equation is based on the observation that the turbidity of the system is directly proportional to the precipitated mass of the polymer.
The relative molecular mass, M assigned to a given precipitant concentration can be calculated from the SCHULTZ equation:

$$M = B/(100\ \varphi - A)$$

where A and B are constants are characteristic of the solvent-polymer precipitant system, φ is the volume fraction of the precipitant. Preliminary calculation of the constants of the equation by modeling the solvation conditions would be theoretically very complicated and unreliable. Therefore, they must be determined in advance experimentally: the test system must first be broken down into separate fractions and their molecular mass determined by an absolute molecular mass method (e.g., ultracentrifuge, osmometry, light scatter measurement). Then, knowing the constants A and B, it is possible to apply the above fast method in practice.
In this practice, the molecular mass distribution of an epoxy resin is characterized by fractional precipitation.

1.3. Preparation and characterization of epoxy resin

An important raw material for crosslinked polymers (duromers) containing relatively large amounts of crosslinks is the epoxy resin. Its spread is due to its wide usability and excellent properties. In combination with crosslinking agents, the epoxy ring in the molecule of the epoxy resin (linear chain alone) opens and bonds to the other molecules, thereby forming a crosslinked structure (under certain conditions, even the hydroxyl groups along the chain can be crosslinked). The resulting crosslinked polymer has excellent mechanical electrical properties and can be widely used, for example, as a material for composite polymers containing other fillers. The chemical basis of the two-component, fast-setting epoxy adhesive is also the linear-chain core resin and the rapid crosslinking after mixing of a hardening component (e.g., polyamines).
Epoxy resin can be prepared in several ways. In one version, diphenyl propane (diane, bisphenol A) is reacted with epichlorohydrin in a strongly alkaline medium containing concentrated sodium hydroxide as shown in Figure 1. By proceeding with the reaction, linear polymer chains can be formed, where the number of members can typically vary from 2 to 25 (Figure 2)

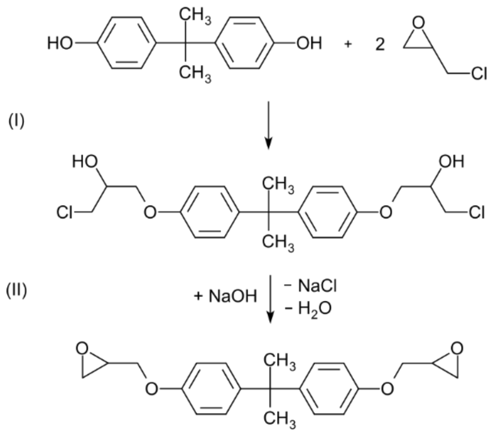

Figure 1 Formation of epoxi prepolymers.

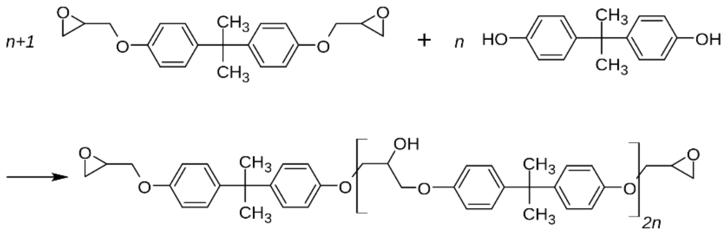

Figure 2 Formation of epoxy polymers

2. Measurements

2.1. Preparation of the polymer solution

Using measuring cylinders (or pipettes), prepare a mixture of 60 cm^3 volume containing 80 v/v% dioxane and 20 v/v% acetone. Use this mixture, prepare a solution of 50 cm^3 of epoxy resin in a volumetric flask with a mass concentration of 0,75 g / dm^3. For faster dissolution, the resin should be pulverized in a mortar before weighing. If the solution is permanently cloudy (indicating that the resin has not been dehydrated properly), choose another sample for making the solution.
Then measure 15 cm^3 of epoxy resin solution into a 100 cm^3 Duran bottle. The precipitant (water) is added into it through the hole in the cap and samples is taken from it for turbidity measurements. Put into it a magnetic stirring bar, as well, because the samples must be stirred continuously.
Plan the amount of precipitant required for successive precipitation. To do this, the relative molecular mass of each possible polymer is to be calculated, knowing the molecular mass of the prepolymer and the repeating unit, if the number of repeating units is between 25 and 2. From the Schulz equation, calculate the volume fraction (φ) of precipitant required to precipitate each fraction and then calculate the volume of water (v) to be added to the 15 cm^3 initial solution to reach the appropriate volume fraction. In the present system, the parameters of the Schulz equation are $B = 1.64 \cdot 10^5$ and $A = 7.3$.

Fill Table 1 based on the calculations.

Number of measurements	Degree of polymerization	$M_{r,polymer}$	φ	v/cm^3
1.	25	…		
2.	24	…		
…	…	…		

Table 1 Measurements

Before starting the measurement, read the instructions for use of the 98703 Hanna turbidimeter and calibrate the instrument with the four calibration standard samples expressed in nephelometric turbidity units (NTU) in the order of 0,1, 15, 100 and 750 respectively. so that the standard samples in the sealed vials are not opened!

Add water to the epoxy resin solution from a burette slowly, dropwise, with continuous stirring, based on the calculated precipitant volumes. Before turbidimetric measurements, stir the system for two minutes after the addition of the precipitant. Then put a sample of 10 cm^3 volumes into the cuvette of the turbidimeter. It is advisable to stir the sample continuously during the measurement, i.e., to have a small magnetic bar in the cuvette and to place the whole turbidimeter on a magnetic stirrer. After reading the turbidity, the samples should be put back into the Duran flask, then the next portion of water added, and at the pre-calculated titration points turbidities should be measured as described above.

2.2. Evaluation

Based on the measurement results, make Table 2.

To calculate m_r, find the maximum value of $\tau \cdot (a + v)$ and divide the other values of $\tau \cdot (a + v)$ by it. The last measured value would not necessarily be the maximum value where the degree of precipitation is complete, so further data could be omitted from the evaluation!

Plot m_r as a function of the corresponding molecular mass values! Differentiate the sum curve and plot the resulting differential molecular mass distribution function!

Measurement	v_{water}/cm^3	$M_{r,polymer}$	τ	$\tau \cdot (a+v)$	m_r	Δm_r	$\Delta m_r / \Delta M$
1.	…	…	…	…	…	…	…
2.	…	…	…	…	…	…	…
…	…	…	…	…	…	…	…

Table 2 Summary of the measurements

Interpret your results. How mono- or polydisperse your system was, what polymerization number was dominant in the sample, etc.

Control questions

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

2. What parameters influence the molar mass distribution of polymer samples?

3. What is a differential distribution function?

4. What is an integral distribution function?

5. What does it mean if a polymer sample is (a) monodisperse, (b) polydisperse, and (c) paucidisperse?

6. Briefly (in 4 to 5 sentences) describe the method of fractional precipitation to determine the molecular mass distribution of the polymer.

7. What is turbidity and how can its measurement be used to determine the relative precipitated polymer mass?

8. What is epoxy resin, how can we produce it? Not the sub-steps, but the names of the characteristic reactants, the type of the reaction and 1 - 2 main features should be mentioned

9. If the expected relative molecular mass of a polymer fraction is 3750, what is the volume of precipitant (water) required for a 15 cm^3 polymer solution according to the Schulz equation if $B = 1.64 \cdot 10^5$ and $A = 7.3$?