

Polymer Science 2024/25

Course Notes of Chapter 1

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1. Introduction

1.1 First Notions of Polymers

A "*polymer*" is an organic or inorganic macromolecular compound resulting from the combination of many molecules of a single "*monomer*" or of different monomers. With "*macromolecules*" one refers to the molecules that constitute a polymeric material, while the term "polymer" is used interchangeably to describe such macromolecules or the material (more exact definitions follow in section 2.1 of this document).

Particularly in case of linear chains, these macromolecules can be very long relative to the size of the individual monomers (on the order of a single nm). Thus, a linear macromolecule made up of thousands of monomers behaves like a more or less flexible string, with a diameter of about 0.5 nm, depending on the case (our example on Slide 12 shows a larger diameter because of the attached side-chain at every second glucose monomer of the main chain), but with a contour length that can exceed 1 μm .

1.2 Plastics: Polymer Materials

There are several broad classes of polymers ranging from natural polymers such as polysaccharides, polypeptides, or DNA, to inorganic glasses, but in this course, we will focus on the polymers that make up organic "*plastics*" and "*rubbers*". Whenever feasible, we may talk about fibers, paints, and adhesives in the broader context of polymer technology or polymer processing techniques.

"Plastics", i.e. solid polymers (usually containing different additives), are used today in a very wide range of products. In 2019, more than 400 million tonnes of plastics, rubbers and other polymeric products were produced worldwide, 80% of which were "**thermoplastics**". Thermoplastics are plastics whose macromolecules are not interconnected (at least not chemically), and which can be transformed into a polymeric melt state by simple heat input without the necessity of any chemical alteration (Slides 36, 53). These materials are characterized by the presence of a glass transition temperature, T_g , and/or a melting temperature, T_m , that are significantly higher than room temperature.

Ca. 5% of plastics are so-called **thermosets** (Slide 40). In general, these are based on monomers (and therefore small molecules) that react with each other by way of forming a macromolecular network, heavily "crosslinked" by covalent bonds. The synthesis has usually to take place during the production of a finished or semi-finished part, because once a thermosetting article is made, it cannot be subsequently reshaped and transformed by adding heat without altering its chemical structure, which would otherwise lead to the loss of its properties. Thermosets are of major importance in the composites industry, as these resins can more easily accommodate reinforcing elements (glass fibers, carbon, etc.) than the comparably large macromolecules of thermoplastic materials.

Moreover, **elastomers** (lightly crosslinked rubbers) differ from thermosets in the amount of such cross-linking points. Due to the much lower cross-linking density, the chain segments between the cross-linking points in elastomers are still long. Elastomers are primarily used as soft solids (in tires, for instance) and based on polymers that display a low glass transition temperature, so that the chain segments remain mobile at the operating temperature. This gives elastomers their characteristic stress-strain behavior along with extraordinary extensibilities (Slides 41, 45). We will devote an entire chapter to this class of polymer materials (Chapter 5.1).

The production of plastics by volume has greatly exceeded that of steel for many years (another 3-4 times more steel is produced by weight, but the density of steel is about 8 g/cm³, which is 8 times that of a typical polymer of about 1 g/cm³) (Slide 16). The majority of plastics is of synthetic origin and derived from petroleum. Note that currently only 1 million tonnes of bioplastics (plastics of biological origin and/or biodegradable) are produced per year. The plastics proliferation is, however, exponentially increasing, and bioplastics' growth is disproportionately high.

1.3 The "Big 5"

The five most used thermoplastics in the world (80% of the thermoplastics market) are polymers made from vinyl monomers, i.e. small molecules containing carbon-carbon double bonds. You find the structures of these polymers on slides 17.

The simplest are the two main types of **polyethylene (PE)**, which are chains of CH_2 groups linked by C-C bonds. A distinction is traditionally made between **high-density polyethylene (HDPE)** and **low-density polyethylene (LDPE)**. They are both "semi-crystalline" polymers containing a mixture of hard crystalline lamellae and soft amorphous regions. We will discuss the difference between HDPE and LDPE later in the class.

The other three are **isotactic polypropylene (PP)**, **atactic polystyrene (PS)**, and **atactic poly(vinyl chloride) (PVC)** (the terms *isotactic* and *atactic* will be discussed later). In these polymers, the $-\text{CH}_2-\text{CH}_2-$ repeat unit of polyethylene is replaced by $-\text{CH}_2-\text{CHX}-$, where X is respectively $-\text{CH}_3$ (methyl), $-\text{C}_6\text{H}_5$ (a benzene ring), and $-\text{Cl}$. Understanding the effect of these changes in chemical structure on the physical properties of the polymer is a primary goal of the upcoming weeks.

1.4 Other Types of Polymers

What do we do with the millions of tonnes of these polymers that we produce each year (Slides 23, 24)? These are all very inexpensive polymers often destined for packaging and end up in the trash. However, there are many other thermoplastics, some of which are shown in Slide 18. Look already at the chemical structures of **poly(ethylene terephthalate) (PET)**, **bisphenol A polycarbonate (PC)**, and **poly(ether ether ketone) (PEEK)**. Do you think that the chains of these polymers are more or less rigid compared to PE? What do you think would be the consequences for their properties?

1.5 Course Objectives

Develop your basic knowledge of the physical and mechanical properties of polymers!

Establish links between the chemical structure and the properties of a given polymer: you will see soon that there are links between the properties of polymers, such as T_m and T_g , and the effect of their chemical structure on their "*rigidity*" or the secondary interactions between chains. We will develop these ideas to the point where you will be able to predict the properties of an unknown polymer at least qualitatively from its structure.

Familiarize yourself with the most common polymers: you have already encountered some of the most important polymers, such as the "Big 5". We will meet them repeatedly throughout this course, and you will know their characteristics, their advantages, and their disadvantages.

2. Definitions and Basic Properties

2.1 Etymology

Polymer: from ancient Greek *πολύς* (a lot) + *μέρος* (part, portion)

Macromolecule: *μακρός* (large) + *molecula* (diminutive of *moles*, or "mass" in Latin)

According to the IUPAC (International Union of Pure and Applied Chemistry) a macromolecule is: "a molecule of relatively high molar mass, the structure of which essentially comprises the multiple repetition of units originating, actually or conceptually, from molecules of low molar mass (the monomers (*μόνος* (alone, isolated)))".

According to some definitions, "a polymer is a substance made up of polymer molecules (macromolecules)", but, as has been said previously, the word polymer is often used to denote the macromolecules themselves. According to Hermann Staudinger, polymers are macromolecules for which chain length differences do not translate into physical property differences, in contrast to small molecules, for which a change in the chemical structure also means a change in their boiling point, melting point, compound polarity, etc. This latter change in property can be exploited to separate different small molecules, but **polymers remain inseparable**.

As we have seen, the *Big 5* as well as many other polymers are synthesized from vinyl monomers with a carbon-carbon double bond, like ethylene (Slides 42, 43). The common name of the polymer is derived from the name of the monomer. This is said to be "polyethylene", even though the constituent repeating unit of the polymer chain is $-\text{CH}_2-$. **The "degree of polymerization", n , therefore, refers to the number of "mers" ($-\text{CH}_2-\text{CH}_2-$ units) in a chain.** In general, we speak of a polymer if $n > 20$, otherwise of an oligomer. We will see later that n and therefore the molar mass must be large if we want to obtain the characteristic resistance and elasticity of a polymer (compare wax and PE - they have identical chemical structures, but you won't be able to make a plastic bag with wax). Finally, **the "catenary" bonds are those which ensure the continuity of the chain.** In the case of PE, these are all C-C bonds, but if you look at Slide 18 you will see other possibilities.

2.2 Chemical Structures

2.2.1 Nomenclature

As already noted in 2.1, in general, "polymonomer" is commonly used to denote a polymer, as well as the corresponding acronym. In case of ambiguity, "poly(monomer)" is sometimes used, e.g., poly(vinyl chloride).

In addition to these common names, the International Union of Physics and Chemistry (IUPAC) defines "systematic" names, which are often used in data compilations, such as *The Polymer Handbook*, and which include end groups. Thus, as shown in Slide 47, PET becomes α -acetyl- ω -

oxymethyl-poly(oxyethyleneoxyterephthaloyl). However, in this course, we will be satisfied with the common name PET thereafter.

2.2.2 Polymer Chain Architectures

Polymers of different shapes can nowadays straightforwardly be synthesized (Slide 35). In our course, we will mostly refer to linear homopolymers (that are composed of just one single repeating unit). These macromolecules can be very long relative to the size of the individual monomers (on the order of a single nm). Thus, a linear macromolecule made up of thousands of monomers behaves like a more or less flexible string, (depending on the case) with a contour length that can exceed 1 μm .

During some syntheses (free radical polymerization, Chapter 6.1), however, branched polymers such as low-density polyethylene (LDPE) are inevitably obtained. Branching greatly determines how materials solidify and, consequently, their mechanical properties. Moreover, 3-dimensional networks are obtained, when chains are cross-linked with each other as in case of elastomeric materials or thermosets.

Our portfolio can easily be extended by way of copolymerization of different monomers, giving rise to, for instance, statistical polymers (a means to obtain amorphous polymer materials), blocky polymers (see for example later in the course: thermoplastic elastomers), or graft polymers (ABS – acrylonitrile butadiene styrene is used by a prominent Danish toy brick manufacturer).

The polymer chain architecture (also often called *microstructure* – we will avoid that term, because it rather describes a materials' structure on the micrometer length scale than the exact chemical composition of a single polymer chain) is defined during its synthesis. It can only be changed upon breakage of covalent bonds.

2.2.3 Configuration

Configuration: the arrangement in three-dimensional space of atoms or groups attached to a central atom. One can only convert one configurational "isomer" to another by breaking covalent bonds. The configuration is therefore built into the polymer chain during the polymerization process as well and it can't be changed afterwards.

Configuration shall not be confused with **conformation (the shape of a molecule that results from rotations around fixed bonds)**. We will talk about conformations in Chapter 3 of the class.

2.2.3.1 Position Isomers

We observe positional isomerism for cases, where a monomer has the possibility of attaching itself to a chain through different atoms in distinct positions. Thus, in the example of Slide 43, a vinyl molecule of the $\text{CH}_2=\text{CHX}$ type can bind to a radical (see Chapter 6.1) through the first or

the second carbon, giving rise to head-to-head, head-to-tail, tail-to-head, or tail-to-tail configurations, even if, in general, one of these configurations (head-to-tail) is strongly favored during an actual radical polymerization.

2.2.3.2 *Cis and Trans Configurations*

The *cis* and *trans* prefixes are used to specify the geometric configuration of a double bond of the polymer backbone by specifying whether the main chain arms of the polymer are located on the same side (*cis*-, "together" in Latin) or on opposite sides (*trans*-, "through" in Latin). Slide 44 shows the example of *cis*-1,4-polyisoprene, a polymer that is chemically identical to natural rubber (NR).

NR contains only the *cis* configuration, so that it is called *cis*-1,4-polyisoprene, not to be confused with *trans*-1,4-polyisoprene, "gutta percha", which is a semi-crystalline polymer. This small change in configuration can have important consequences for the properties (Slide 45). The *trans* configuration allows the chain to adopt a very linear "zig-zag" conformation, which favors the stacking of molecules in crystal form. The *cis* configuration, however, disrupts the linearity of the polymer chain in its outstretched conformation, which renders crystallization more difficult. In fact, at room temperature, NR crystallizes only when it is very deformed so that the polymer chains become stretched. Crosslinked (vulcanized) NR not only behaves as an elastomer at room temperature but self-reinforces by crystallizing at large deformations. A true marvel of macromolecular engineering. But what does a plant use of this behavior for?

2.2.3.3 *Tacticity*

Consider a vinyl polymer with an X substituent in head-tail configuration and in "zig-zag" conformation, i.e. a fully outstretched chain, as shown on Slide 46. We see that the substituents R can all be on the same side of the chain (the "isotactic" configuration), alternate from side to side (the "syndiotactic" configuration) or adopt random positions (the "atactic" configuration). By insertion polymerization (Chapter 6.1) one can control the tacticity and therefore obtain a regular configuration. A regular configuration from either isotactic or syndiotactic configured polymers is generally more compatible with the notion of crystallization, or the formation of a periodic structure, than an atactic configuration, which can be considered as more irregular. Therefore, isotactic PP can crystallize, while atactic PP, as well as atactic PS and PVC do not crystallize. Since PS and PVC are glassy polymers, this does not have too much of an impact on their room temperature properties. But it was not until the discovery of the insertion polymerization in 1953 (which won the Nobel Prize for Karl Ziegler and Guido Natta) that semicrystalline isotactic PP could be made, which is therefore solid at room temperature and only for this reason could join the *Big 5*.

2.3 Molar Masses of Polymers

The interesting and useful mechanical properties (for instance, rubber elasticity, mechanical strength, viscosity) that are uniquely associated with polymer materials are a consequence of their high molecular weight. However, contrary to a well-defined small molecule such as those you have synthesized during the lab course, a precise molar mass cannot be assigned to a polymer. Polymers are heterogeneous in molecular weight, they are **polydisperse**, that is polymers are mixtures of molecules of different molecular weight. In fact, most polymerization reactions produce rather broad molar mass distributions that vary depending on the polymerization conditions and certain statistical processes involved in the underlying polymerization mechanism.

2.3.1 Definitions of Average Molar Masses and Dispersity

It is often important to control and to well characterize the molecular weight distribution to obtain and improve certain desired physical properties in a polymer product. While it is possible to determine the molar mass¹ distribution of a polymer, $\phi(M)$, using, for example, chromatographic techniques, it is generally more practical to characterize this distribution in terms of different "**moments**", which correspond to different definitions of the average molar mass. In general, the k^{th} moment, μ^k , of the number fraction distribution is defined as the sum of the products of the number fraction n_x of chains with a degree of polymerization x and the corresponding molar mass M_x raised to the k^{th} power:

$$\mu_k = \sum_x n_x M_x^k \quad (1).$$

By definition, the zeroth moment ($k = 0$) is equal to unity. The first moment ($k = 1$) characterizes the mean of the distribution and the second moment ($k = 2$) is its variance.

The simplest average molar mass is the **number average molar mass**, M_n , defined as the ratio of the first to zeroth moments of the number fraction distribution, which is equivalent to the sum of all the molar masses of the chains present in the polymer, divided by the total number of chains. Let x be the degree of polymerization; n_x the number of macromolecules with degree of polymerization x ; M_x the mass of such macromolecules; and M_0 the mass of a monomer:

$$M_n = \frac{\sum_{x=1} n_x M_x}{\sum_{x=1} n_x} = \frac{\sum_{x=1} n_x x M_0}{\sum_{x=1} n_x} \quad (2).$$

¹ The term *molar mass* will be preferred here. It is equivalent to the mass of a mole of a particular substance and therefore expressed in g/mol. In contrast, *molecular weight* is equivalent to the 1/12 of the ratio of the mass of a molecule to the atomic mass unit of a C^{12} atom and has no units. One finds, however, that both terms are often used interchangeably.

M_n is relatively easy to be determined, and often listed on a chemical bottle of a polymer. However, M_n is not necessarily very representative because it overrepresents low mass chains. Consider, for example, a polymer made up of only two chains of masses M_1 and $M_2 \ll M_1$. The number average molar mass will be close to $M_1/2$, even though M_2 is insignificant in determining the properties of this mixture. Therefore, the **weight-average molar mass, M_w** , is often preferred, which is defined as the ratio of the second moment to the first moment of the number fraction distribution, which gives a greater bias to high molar mass chains:

$$M_w = \frac{\sum_{x=1} w_x M_x}{\sum_{x=1} w_x} = \frac{\sum_{x=1} n_x M_x^2}{\sum_{x=1} n_x M_x} = \frac{\sum_{x=1} n_x^2 M_0}{\sum_{x=1} n_x x} \quad (3),$$

where w_x is the weight of macromolecules with a degree of polymerization x . By definition, $M_w \geq M_n$. Their ratio defines the **dispersity, $\mathcal{D}$** (formerly known as polydispersity or polymolecularity; in textbooks, you also find the symbol I or P), which is a measure of the width of the molar mass distribution, and is given by

$$\mathcal{D} = \frac{M_w}{M_n} \quad (4).$$

Note that $\mathcal{D}$ is close to 1 for a very narrow molar mass distribution where all the chains have roughly the same length (a nearly monodisperse system), but $\gg 1$ if the distribution is very broad. Note also that the herein discussed values strongly depend on the polymerization method (see Chapter 6.1).

2.3.2 How Important is the Molar Mass of a Polymer?

The remarkable and unique properties of polymers are due to the large size of their chains.

- Structural implications:
 - As a consequence of their high molar mass, polymers capable to crystallize do that only partially (semi-crystalline polymers).
 - Great parts of polymers remain amorphous and vitrify at the glass transition temperature that is a function of the molar mass as well.
 - Polymers do not exhibit a gaseous phase.
- Processability, like a common capability of film and fiber formation from the molten state:
 - High viscosity in both solution and in the molten state
 - Prominent viscoelastic behavior
- Mechanical properties:
 - Rubber elasticity

- Plastic deformation
- Polymer chain entanglement and mechanical resilience in tensile deformation

It is therefore essential to know how the molar mass distribution, average masses, and dispersity depend on the nature of the synthetic method. For selected polymerization mechanisms, this will be explained in Chapter 6.1. Perhaps, we will also briefly review some experimental methods to characterize one or more of these quantities.

3. Summary

- Polymers, macromolecules: recognized in the 1920's that they consist of covalently bonded repetitive sequences of subunits derived from monomers
- Characterized by a molecular weight distribution instead of a defined molar mass
- Polymer chemical structures defined by:
 - Composition
 - Configuration (isomers)
 - Architectures
 - Copolymers
 - Branching, crosslinking etc.
- First systematic synthesis in 1938 (Nylon 6,6).