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Polymer Science 2025/26

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 formed by the combination of many repeating units, called *monomers*. Depending on the chemistry, a polymer may be made from a single type of monomer or from several different monomers. The term *macromolecule* refers specifically to the individual molecules that make up a polymer, whereas the word *polymer* is often used interchangeably to describe either these macromolecules or the bulk material (more precise definitions will follow in Section 2.1).

In the case of **linear polymers**, macromolecules can reach enormous lengths compared to the nanometer-scale size of their monomer units. Thus, a single linear chain built from thousands of monomers behaves like a more or less flexible string with a typical diameter of about 0.5 nm (though larger if bulky side groups are present). Its contour length can exceed 1 µm, i.e. thousands of times larger than an individual monomer.

1.2 Plastics: Polymer Materials

Polymers exist in many forms ranging from natural biopolymers (polysaccharides, polypeptides, DNA) to inorganic glasses (silica glasses). In this course, however, our main focus will be on **organic polymers used as plastics and rubbers**. Whenever useful, we will also touch on fibers, paints, and adhesives in the broader context of polymer technology or polymer processing techniques.

Today, plastics are ubiquitous. By volume, their annual production has long surpassed that of steel. By weight, however, steel still dominates by a factor of 3–4 due to its higher density (~8 g/cm^3 compared to **~1 g/cm^3 for typical plastics**). In 2019, global production of polymeric materials (plastics, rubbers) exceeded 400 million tonnes. Most plastics are derived from petroleum, but a small yet rapidly growing fraction are bioplastics (plastics of biological origin and/or biodegradable). Current production is ~1 million tonnes per year, but growth rates are disproportionately high compared to conventional plastics.

Thermoplastics make up the majority (~80%) of plastic materials. They consist of macromolecules that are not chemically interconnected, which makes their processing reversible and highly versatile. Thermoplastics are characterized by a glass transition temperature, T_g, and/or a melting temperature, T_m, (Slides 71, 72). Glassy polymers show a T_g well above room temperature, while semicrystalline polymers can be operated in their solid state up to their T_m.

Thermosets (~5% of plastics) are formed from low-molecular precursors that chemically react to build up a heavily **crosslinked network**. Because this network is permanent, a cured thermoset cannot be reshaped by heating, why their synthesis has usually to take place during the production of a finished or semi-finished part. 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 (Slides 72).

Elastomers (lightly crosslinked rubbers) occupy an intermediate category. They are lightly crosslinked networks of polymers in their rubbery state in which chain segments between crosslinks are still very long and flexible. Elastomers are based on polymers with low T_g values to ensure segmental mobility at service temperatures. This molecular design gives elastomers their remarkable **elastic extensibility** and characteristic stress-strain behavior (Slides 65, 72, 78). We will return to elastomers in detail in Chapter 4.1.

1.3 The "*Big 5*"

Five thermoplastics dominate the global market, together making up ~80% of thermoplastic production). All five are derived from vinyl monomers (small molecules containing C=C double bonds) and are exclusively based C–C **catenary bonds** (those bonds that provide the continuous backbone of the polymer chain). Their chemical structures are shown on Slide 18.

- **polyethylene (PE):** the simplest polymer, consisting only of $–CH_2–$ units. Two major types exist: **high-density polyethylene (HDPE)** and **low-density polyethylene (LDPE)**. Both are "semi-crystalline" polymers containing a mixture of rigid crystalline lamellae and soft amorphous regions. Their key differences will be discussed later in the course.
- **isotactic polypropylene (iPP):** derived from propylene, with a pendant $–CH_3$ group.
- **atactic polystyrene (PS):** derived from styrene with a pendant phenyl group.
- **poly(vinyl chloride) (PVC):** derived from vinyl chloride, with a pendant –Cl group. PVC is usually atactic as well.

We will learn how these small changes in chemical structure (changes from –H to $–CH_3$, to $–C_6H_5$, to –Cl per repeat unit) drastically alter their physical properties, which is one of the central themes of this course.

1.4 Other Types of Polymers

What happens to the millions of tonnes of commodity polymers produced each year? Many end up in short-lived applications like packaging, and thus in waste streams (Slides 22–27).

But the polymer world extends far beyond cheap, disposable plastics. Consider, for example, polyesters like **poly(ethylene terephthalate) (PET)**, **polycarbonate (PC)**, and high-performance polymers like **poly(ether ether ketone) (PEEK)**. Compared to PE, these polymers contain rigid aromatic or heteroatom-rich backbones. Consequently, are these chains more or less flexible than those of PE? How might this rigidity affect thermal and mechanical properties? We will build intuition for these relationships in the weeks ahead.

1.5 Course Objectives

By the end of this course, you should be able to:

- **understand the basic physical and mechanical properties of polymers.**
- **establish links between chemical structure and macroscopic properties:** For example, how side groups, backbone rigidity, or intermolecular interactions affect T_g and T_m, crystallinity, and mechanical behavior.
- **recognize the most common polymers** (starting with the Big Five), their advantages, and their limitations.
- **predict qualitatively** the properties of an unknown polymer based on its chemical structure.
- **make suggestions for materials selection and processing.**

2. Definitions and Basic Properties

2.1 Etymology, IUPAC Definition, and Staudinger's Concept

The word **polymer** comes from the Greek *πολύς* (*polys* = many) and *μέρος* (*meros* = part or unit). A polymer is therefore literally a material made of "many parts".

The related term **macromolecule** combines Greek *μακρός* (*makros* = large) with the Latin diminutive *molecula* (from *moles* = mass).

According to the International Union of Pure and Applied Chemistry (IUPAC), 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).*"

In strict terminology a polymer is a substance consisting of macromolecules. A macromolecule is an individual molecule within that substance. However, in everyday scientific language, "polymer" is often used to refer to both the material and the molecules it is made of.

The modern concept of polymers was introduced by **Hermann Staudinger** in the 1920s. He emphasized that polymers are not aggregates of small molecules but genuine **covalently bonded repeat units**. For polymers, once the chain length exceeds a certain threshold, further increases do not change the physical properties significantly, while for small molecules, even tiny changes in chemical structure strongly affect physical properties such as boiling point, melting point, or polarity. Therefore, we cannot easily separate individual polymer chains, **polymers remain inseparable**.

The **degree of polymerization, *n*,** refers to the number of repeat units in a chain. In general, we typically call a material a polymer when $n > 20$, shorter chains are called **oligomers**. The chain length (and thus the molar mass) has a dramatic effect on properties: For example, paraffin wax (n ~20–50) and polyethylene (n in the thousands) have identical chemical structures. But wax is brittle and crystalline. You cannot make a plastic bag out of it. By comparison, PE is tough, flexible, and processable (Slide 67).

2.2 Chemical Structures

2.2.1 Nomenclature

- In practice, polymers are usually named by attaching the prefix "**poly**" to the monomer name, e.g. *polyethylene*.
- To avoid ambiguity, parentheses are used: **poly(vinyl chloride)** instead of "polyvinyl chloride)
- Abbreviations are common: PE, PP, PVC, PS, PET.
- IUPAC systematic names are much more detailed and include end groups. In this course we will mostly use the common names and abbreviations.

2.2.2 Polymer Chain Architectures

Polymers can adopt very different chain architectures (Slide 34):

- **linear homopolymers**: one repeating unit only (e.g. PE, PS). These chains can be extremely long (contour lengths > 1 µm).
- **branched polymers**: e.g. LDPE, formed during radical polymerization. Branching affects crystallinity and mechanical properties.
- **crosslinked polymers**: chains are chemically tied together in a 3D network (see elastomers and thermosets)
- **copolymers** made from two or more monomers
    - **statistical copolymers:** random arrangement of the monomers, often amorphous.
    - **block copolymers**: long sequences of each monomer type.
    - **graft copolymers**: side chains of one polymer grafted onto another backbone (e.g. ABS, used in LEGO® bricks)

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 fixed during synthesis and can only be changed by breaking covalent bonds.

2.2.3 Configuration

Configuration: 3D arrangement of atoms/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.

Do not confuse with **conformation (the shape of a molecule that results from rotations around fixed bonds)**, which we will cover in Chapter 2.

Position Isomers:

- occurs when a monomer can add to a chain in different ways.
- Example: vinyl monomers of the CH_2=CHX can add through either carbon, leading to head-to-tail, head-to-head, etc. (Slide 62). In practice, **head-to-tail** addition dominates during radical polymerization.

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).

- *cis*-1,4-polyisoprene = natural rubber (NR), amorphous, used in elastomers.
- *trans*-1,4-polyisoprene = "gutta percha", semi-crystalline, rigid.

This small change in configuration can cause huge property differences (Slide 65). The *trans* configuration allows the chain to adopt a highly linear "zig-zag" conformation, which favors crystallization. By contrast, the *cis* configuration, cannot be easily packed and only crystallizes at room temperature when stretched (in fact, crosslinked (vulcanized) NR not only behaves as an elastomer but self-reinforces due to its crystallization at large deformations, a true marvel of macromolecular engineering).

Tacticity

Tacticity is relevant for polymers based on unsymmetric vinyl monomers (Slide 63).

- **isotactic**: all substituents X are located on the same side of the backbone chain.
- **syndiotactic**: all X alterante sides.
- **atactic**: random arrangement of X.

Tacticity determines crystallinity (see Chapter 3.3)**!** The control over tacticity is possible with insertion polymeriaztion (Ziegler-Natta catalysts, Nobel prize 1963, Chapter 6.1).

2.3 Molar Masses of Polymers

The defining feature of polymers is their very large molar mass, which underlies virtually all of their outstanding properties. **The unique mechanical properties of polymers** (such as rubber elasticity, chain entanglement, high viscosity, toughness, and the ability to form fibers and films) **arise from their very large molar masses.**[1] Unlike small molecules, however, polymers cannot be described by a single precise molar mass: every synthesis involves statistical processes that produce a mixture of chains of different lengths, i.e. a **molar mass distribution**. Polymers are therefore **polydisperse** (Slide 39). **The distribution is commonly characterized by the number-average molar mass, M_n, the weight-average molar mass, M_w, and their ratio, the dispersity Đ, which measures the breadth of the distribution.** The shape and width of this distribution depend strongly on the polymerization mechanism (compare, for example, Slides 47 and 57). *Step-growth* and *chain-growth polymerizations*, as well as *living and controlled polymerization* are treated in detail in the Readers on the Moodle page. The definitions and derivations of M_n, M_w, and Đ can likewise be found in the Reader on *Molar Masses*.

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[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.

3. Characterization of Polymers

A comprehensive understanding of a polymer requires characterization of its chemical structure, molar mass, thermal behavior, and mechanical properties. A few selected methods are shown on Slides 74–78.

- **Gel Permeation Chromatography (GPC):** a dilute polymer solution is passed through a column filled with a microporous gel. Large chains elute faster than small ones, since they cannot easily penetrate the pores. Calibration with polymers of known molar mass yields the entire molar mass distribution. With advanced “triple detection” (refractometry, viscometry, light scattering), even universal calibration across different architectures is possible.
- **Differential Scanning Calorimetry (DSC):** measures heat flow during heating or cooling (including effects of processing history). DSC provides glass transition temperature, melting temperature, and crystallinity which are key parameters for thermal and structural behavior.
- **Rheology**: probes the flow and deformation of polymer melts or solutions. Due to polymer chains entanglements, polymers exhibit pronounced viscoelasticity, which can be quantified in shear or oscillatory tests. Rheological properties are fundamental for assessing processability.
- **Universal Testing Machine (UTM):** measures macroscopic mechanical properties such as tensile strength, Young’s modulus, elongation-at-break, and toughness. These properties reflect the interplay between chain architecture, morphology, and processing history.