Lecture 6.

Theme. Stepwise processes of formation of macromolecules. Polycondensation. Kinetics and mechanism of polycondensation.

Aim: generate the following learning outcomes:
-formulate the main types of polycondensation
-list the stages of polycondensation processes
-describe the methods of polycondensation reactions; advantages and disadvantages of each
-to order the main side reactions in equilibrium polycondensation

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Purpose:

To study the step-growth (stepwise) formation of macromolecules, focusing on the principles, mechanism, and kinetics of polycondensation as a major method for synthesizing condensation polymers.

Lecture content:
Polycondensation. Types of polycondensation reactions.
The main differences between polymerization and polycondensation processes.
Thermodynamics of polycondensation and polycondensation equilibrium.
Molecular weight and molecular mass distribution during polycondensation.
Kinetics of polycondensation.
Conducting polycondensation in the melt, in solution and at the phase interface.

Main Questions:

1. What is step-growth (stepwise) polymerization?
2. What is polycondensation and how does it differ from addition polymerization?
3. What are the main stages and mechanism of polycondensation?
4. What factors affect the kinetics of polycondensation?
5. What are the industrial and practical applications of condensation polymers?

Key Theses:

1. Stepwise (Step-Growth) Polymerization — General Concept

- **Stepwise polymerization** (or **step-growth polymerization**) is a process in which macromolecules are formed by a series of successive reactions between **bifunctional or polyfunctional monomers**.
- Unlike chain-growth polymerization, where growth occurs at active centers, in stepwise polymerization **any two reactive species (monomers, dimers, trimers, etc.)** can react with each other.
- The molecular weight of the polymer increases gradually as the reaction proceeds.

2. Polycondensation — Definition

- **Polycondensation** is a type of step-growth polymerization in which monomers react with the **elimination of small molecules** such as water (H_2O), hydrogen chloride (HCl), ammonia (NH_3), or methanol (CH_3OH).
- Each condensation step forms a new **covalent bond** between monomer units, while a small by-product molecule is released.

Examples of polycondensation reactions:

- Formation of **polyesters** from diacids and diols:
- Formation of **polyamides** (e.g., nylon):
- Formation of **phenol-formaldehyde resins** and **urea-formaldehyde resins** by condensation of monomers with formaldehyde.

3. Mechanism of Polycondensation

Polycondensation typically occurs in **three main stages:**

1. **Initial stage (oligomer formation):**
   - Monomers combine to form dimers, trimers, and short oligomers.
   - The reaction may proceed through intermediate steps like esterification or amidation.
2. **Growth stage:**
   - Oligomers react with each other to form longer chains.
   - Each reaction releases a small molecule (e.g., H_2O or HCl).
   - Molecular weight increases progressively.
3. **Final stage (macromolecule formation):**

    - High molecular weight polymers are formed when the degree of polymerization approaches completion.
    - The system often becomes highly viscous, and diffusion of monomers becomes slower.

4. Kinetics of Polycondensation

- **Stepwise kinetics:**
    - Any two reactive molecules can react; thus, reaction rate depends on the **concentration of functional groups** rather than on chain length.
    - The reaction follows **second-order kinetics** in the early stages.
    - Where ([C]) is the concentration of reactive functional groups and (k) is the rate constant.
- **Degree of polymerization (DP):**
    - The **Carothers equation** relates the average degree of polymerization to the **fractional conversion (p)** of functional groups.
    - High molecular weights are achieved only when (p) is very close to 1 ($\geq$ 0.99).
- **Temperature and catalysts** strongly influence the reaction rate.
    - Higher temperatures accelerate the reaction but may also lead to side reactions or degradation.
    - Catalysts (e.g., acids, bases, metal salts) are often used to increase reaction efficiency.

5. Factors Affecting Polycondensation

- **Monomer functionality:** monomers must have at least two reactive groups.
- **Reaction equilibrium:** since condensation reactions are often reversible, the removal of by-products (e.g., water) drives the reaction forward.
- **Temperature and pressure:** higher temperatures promote reaction; vacuum helps remove volatile by-products.
- **Catalysts:** enhance reaction rate and selectivity.
- **Stoichiometric balance:** slight excess of one reactant can limit chain growth and reduce molecular weight.

6. Industrial and Practical Importance

- **Polycondensation** is widely used to produce important polymers:
    - **Polyesters** (e.g., polyethylene terephthalate — PET) for fibers, films, and bottles.
    - **Polyamides** (e.g., nylon-6,6) for textiles and engineering plastics.
    - **Polycarbonates** for optical materials and impact-resistant plastics.

- **Phenol-formaldehyde and urea-formaldehyde resins** for adhesives and coatings.

- These polymers are known for their **thermal stability, mechanical strength, and chemical resistance**.

Control Questions:

1. What is the main difference between step-growth and chain-growth polymerization?
2. List the main mechanisms of reactions of stepwise growth of macromolecules.
3. Define polycondensation and give examples of typical condensation reactions.
4. Write in general the equilibrium constant of the polyamidation reaction.
5. Describe the main stages of polycondensation.
6. Write the Carothers equation and explain its meaning.
7. What factors affect the rate and extent of polycondensation?
8. Why is the removal of by-products important in polycondensation?
9. List the factors affecting the molecular weight of polymers synthesized by equilibrium polycondensation.
10. List several industrial polymers obtained by polycondensation.

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