

Lecture 3.

Theme. Synthesis of polymers. Radical polymerization.

Aim: generate the following learning outcomes:

- formulate the main processes of chain polymerization;
 - to determine the types of chain breakage in various variants of chain polymerization;
 - determine the type of polymerization (radical);
 - to find the relationship of kinetic parameters of radical polymerization with the molecular weight of polymers;
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Purpose:

To study the main methods of polymer synthesis, focusing on the mechanism, stages, and characteristics of radical polymerization as one of the most important industrial processes in polymer chemistry.

Lecture content:

Classification of the main methods for obtaining polymers.

Polymerization. Thermodynamics of polymerization. The concept of polymerization-depolymerization equilibrium.

Classification of chain polymerization processes.

Radical polymerization. Initiation of radical polymerization. Types of initiators.

Reactions of growth, breakage and transmission of the chain.

Kinetics of radical polymerization at low degrees of transformation.

Molecular weight and molecular mass distribution of polymers formed during radical polymerization.

Polymerization at deep degrees of transformation.

Main Questions:

1. What are the main methods of polymer synthesis?
2. What is the principle of radical polymerization?
3. What are the stages of radical polymerization?
4. Which factors influence the rate and yield of radical polymerization?
5. What are the advantages and limitations of this method?

Key Theses:

- **Polymer synthesis** refers to the chemical processes by which monomers are converted into polymers.
- The two main methods are:
 1. **Addition polymerization** — monomers add to each other without forming by-products (e.g., radical, ionic, coordination polymerization).
 2. **Condensation polymerization** — monomers react with the elimination of small molecules (e.g., water, HCl).

Radical Polymerization

- **Definition:** Radical polymerization is a type of chain-growth polymerization where the active center is a free radical — a molecule or atom containing an unpaired electron. This method is used to produce important industrial polymers such as polyethylene, polystyrene, PVC, and PMMA (plexiglass).

Stages of Radical Polymerization:

1. **Initiation:**
 - Formation of free radicals by decomposition of an **initiator** (e.g., benzoyl peroxide, AIBN).
 - The radical reacts with a monomer molecule, forming an active radical center that begins chain growth.
2. **Propagation (chain growth):**
 - The active radical adds new monomer molecules, extending the chain and transferring the radical center to the chain end.
3. **Termination:**
 - The reaction stops when two radicals combine or disproportionate, destroying the active centers.
 - **Combination:** Two growing macroradicals – kinetic chains form one material chain by making a bond between active centers.
 - **Disproportionation:** One radical transfers a hydrogen atom to another, forming a saturated and an unsaturated polymer end.
4. **Chain Transfer (optional stage):**
 - The active radical can transfer its activity to another molecule (monomer, solvent, or polymer), affecting molecular weight and branching.

Factors Influencing Radical Polymerization:

- **Temperature** — affects initiator decomposition rate and polymerization speed.
- **Concentration of initiator** — higher initiator concentration increases radical formation but decreases average molecular weight.
- **Monomer structure** — electron-donating or withdrawing substituents influence radical stability.
- **Presence of inhibitors** (oxygen, hydroquinone) — can stop polymerization by neutralizing radicals.

Characteristics of Radical Polymerization:

- High reaction rate.
 - Suitable for a wide range of monomers with double bonds (vinyl monomers).
 - Can occur in bulk, solution, suspension, or emulsion.
 - Produces polymers with relatively broad molecular weight distribution (high polydispersity).
 - Mechanism is not highly selective, so structural control is limited.
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Control Questions:

1. What are the two main types of polymer synthesis?
 2. Define radical polymerization.
 3. What are the main stages of radical polymerization?
 4. What is the role of an initiator in radical polymerization?
 5. List the main methods of initiating radical polymerization.
 6. How can radical polymerization be terminated?
 7. What factors influence the rate and molecular weight of the resulting polymer?
 8. Name the factors affecting the length of the macromolecules formed during radical polymerization in mass.
 9. What are the main advantages and limitations of radical polymerization?
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