Lecture 4.

Theme. Ionic polymerization. Cationic polymerization and anionic polymerization, kinetics.

Aim: generate the following learning outcomes:
- determine the type of polymerization (anionic, cationic, ion-coordination);
-to determine the types of chain breakage in various variants of ion polymerization;
- to find the relationship between the conditions of ion polymerization with the structure of synthesized polymers;

Purpose:
To study the mechanisms, conditions, and kinetic characteristics of ionic polymerization, focusing on the differences between cationic and anionic processes and their industrial significance.

Lecture content:
Cationic polymerization.
Characteristics of monomers capable of entering into cationic polymerization.
Catalysts and co-catalysts.
Growth and restriction of chain growth during cationic polymerization.
The influence of the nature of the solvent.
Kinetics of the process.
Anionic polymerization.
Characteristics of monomers capable of entering into anionic polymerization.
Catalysts of anionic polymerization.
Initiation, growth and restriction of chain growth during anionic polymerization. "Living chains".
Features of ionic polymerization of cyclic monomers.

Main Questions:

1. What is ionic polymerization?

2. What are the main features of cationic and anionic polymerization?
3. What are the stages of each mechanism?
4. Which factors affect the kinetics of ionic polymerization?
5. What are the advantages and limitations of ionic polymerization methods?

Key Theses:

1. General Definition

- **Ionic polymerization** is a type of **chain-growth polymerization** in which the reactive center is an **ion** rather than a free radical.
- It occurs through **ionic mechanisms** — either **cationic** (positively charged active center) or **anionic** (negatively charged active center).
- These polymerizations typically require **high-purity monomers**, **non-protic solvents**, and **absence of water or oxygen**, since ions are easily neutralized.

2. Cationic Polymerization

- **Active center:** positively charged carbocation.
- **Initiators:** Lewis acids or strong protonic acids — e.g. $AlCl_3$, BF_3, $TiCl_4$, H_2SO_4, HCl.
- **Typical monomers:** those containing electron-donating groups that stabilize a positive charge — e.g. isobutylene, styrene, vinyl ethers.

<u>Stages of cationic polymerization:</u>

1. **Initiation:**
   - Formation of a carbocation by protonation or complex formation.

2. **Propagation:**
   - The carbocation reacts with a monomer molecule, forming a longer chain with a new cationic center.

3. **Termination:**
   - By combination with a counterion or nucleophile, or by chain transfer.

Features:

- Extremely sensitive to impurities (moisture, oxygen).
- Occurs rapidly at low temperatures.
- Produces polymers like polyisobutylene and butyl rubber.

3. Anionic Polymerization

- **Active center:** negatively charged carbanion.
- **Initiators:** strong bases or organometallic compounds — e.g. $NaNH_2$, butyllithium (BuLi), Grignard reagents.
- **Typical monomers:** those with electron-withdrawing groups that stabilize a negative charge — e.g. acrylonitrile, methyl methacrylate, styrene, butadiene.

Stages of anionic polymerization:

1. **Initiation:**
    - The initiator donates an electron or a negative ion to the monomer.

2. **Propagation:**
    - The carbanion reacts with additional monomers, extending the chain.

3. **Termination:**
    - Often **does not occur spontaneously** — unless deliberately stopped by impurities or added reagents.
    - Hence, many anionic polymerizations are **"living polymerizations"**, meaning chains keep growing until quenched.

Features:

- Allows precise control of molecular weight and narrow distribution (low polydispersity).
- Can be used to create block copolymers by sequential monomer addition.
- Requires extremely pure, inert conditions.

4. Kinetics of Ionic Polymerization

- **Cationic polymerization kinetics:**
    - The rate depends on monomer concentration, type of initiator, and counterion stability.
    - Termination can occur by various fast side reactions, making the process complex.
- **Anionic polymerization kinetics:**

- Often exhibits **zero-order kinetics** with respect to initiator in living systems.
- Molecular weight increases linearly with conversion if no termination occurs.

Factors affecting kinetics:

- Solvent polarity and dielectric constant (affect ion-pair stability).
- Temperature (affects ion dissociation and propagation rates).
- Monomer structure (electron-donating or withdrawing groups).
- Presence of impurities or proton donors (which terminate chains).

5. Comparison of Cationic and Anionic Polymerization

Feature	Cationic Polymerization	Anionic Polymerization
Active center	Carbocation (+)	Carbanion (–)
Initiators	Acids, Lewis acids	Bases, organometallics
Suitable monomers	Electron-donating	Electron-withdrawing
Sensitivity	Sensitive to nucleophiles	Sensitive to electrophiles
Termination	Common	Rare (living system)
Control of MW	Limited	Excellent
Examples	Polyisobutylene, vinyl ethers	Polystyrene, polybutadiene

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Control Questions:

1. What is ionic polymerization and how does it differ from radical polymerization?
2. Explain the role of the medium in ionic polymerization. List the possible types of active centers in ionic polymerization.
3. Give examples of the main types of anionic and cationic initiators of ion polymerization.
4. Describe the stages of cationic polymerization.
5. What types of monomers and initiators are used in cationic polymerization?
6. Describe the mechanism of anionic polymerization.
7. What does “living polymerization” mean and why is it important?
8. Name the main conditions of "living" polymerization.
9. What factors influence the kinetics of ionic polymerization?

10. Compare cationic and anionic polymerization in terms of mechanisms and applications.

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