

Lecture 3.

Theme. Features of the polymer state of the substance. Configuration and conformation of polymers.

Aim: generate the following learning outcomes:

- to relate substances to high-molecular compounds with the manifestation of properties due to large size and chain structure;
 - distinguish polymers of the same composition with different spatial arrangement of repeating links;
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Purpose:

To understand the structural features that define the polymer state of matter, and to study the concepts of **configuration** and **conformation**, which determine the physical and mechanical properties of polymers.

Lecture content:

The most important properties of polymer substances due to the large size, chain structure and flexibility of macromolecules.

Macromolecule configuration and configuration isomerism.

Local and configuration isomers in macromolecules of polymers of monosubstituted ethylenes and dienes.

Stereoisomerism and stereoregular macromolecules. Isotactic and syndiotactic polymers.

Conformational isomerism and conformation of a macromolecule.

Ordered conformations of isolated macromolecules (polypeptides, proteins, nucleic acids).

Polymer-polymer complexes of synthetic and natural polymers. Cooperative conformational transformations.

Main Questions:

1. What are the main features of the polymer state of matter?
 2. What is the difference between configuration and conformation in polymer molecules?
 3. How do molecular structure and flexibility affect polymer properties?
 4. What types of configurations and conformations are possible?
 5. How are these structural features related to the physical behavior of polymers (elasticity, crystallinity, etc.)?
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Key Theses:

1. Features of the Polymer State of Matter

- The **polymer state** is a distinct state of condensed matter characterized by the presence of **macromolecules**—giant chains consisting of thousands of repeating units (monomers).
- Unlike low-molecular substances, polymers exhibit **unique physical properties** due to their chain structure, entanglement, and intermolecular interactions.
- The polymer state combines features of **solids** and **liquids**:
 - At certain conditions, polymers behave as **viscoelastic materials** — showing both elastic (solid-like) and viscous (liquid-like) responses.
 - The transition between these behaviors depends on **temperature**, **molecular weight**, and **degree of crystallinity**.

Distinctive characteristics of the polymer state:

- Very high molecular weight.
- Chain-like molecular structure.
- Existence of **amorphous** and **crystalline** regions.
- Slow molecular motion and relaxation processes.
- Dependence of properties on time and temperature (viscoelasticity).

2. Configuration of Polymers

- **Configuration** refers to the **permanent spatial arrangement** of atoms in a polymer chain that **cannot be changed without breaking chemical bonds**.
- It is determined by the **sequence and stereochemistry** of monomer units along the chain.
- The configuration defines the **stereoregularity** of the polymer, which influences crystallinity and mechanical properties.

Main types of polymer configuration:

1. **Linear configuration** — polymer chains without branches (e.g., HDPE).
2. **Branched configuration** — side chains attached to the main backbone (e.g., LDPE).
3. **Cross-linked (network) configuration** — polymer chains interconnected by covalent bonds (e.g., vulcanized rubber).

Stereochemical configurations (tacticity):

- **Isotactic:** all substituents arranged on the same side of the chain.
- **Syndiotactic:** substituents alternate sides regularly.
- **Atactic:** random arrangement of substituents.

The **tacticity** directly affects **crystallinity** and **melting behavior** — isotactic and syndiotactic polymers crystallize easily, while atactic ones remain amorphous.

3. Conformation of Polymers

- **Conformation** describes the **spatial arrangement** of atoms in the polymer chain that can **change by rotation** around single (σ) bonds **without breaking covalent bonds**.
- Because of this rotational freedom, polymer chains can adopt many conformations, leading to flexible and dynamic molecular structures.
- Conformational transitions are important for elasticity, folding, and chain packing in solids.

Common conformations:

- **Trans** and **gauche** conformations (in simple hydrocarbon chains).
- **Helical conformations** (e.g., in proteins or isotactic polypropylene).
- **Random coil** — characteristic of flexible polymer chains in solution or amorphous state.

The **conformational flexibility** of polymer chains determines their **entropy elasticity** — the ability to stretch and return to original shape, as in rubber.

4. Relationship Between Configuration, Conformation, and Polymer Properties

- **Configuration** is permanent and defines the polymer's *chemical identity* and *stereoregularity*.
- **Conformation** is variable and defines the *physical state* and *mobility* of polymer chains.

- Together, they determine:
 - **Crystallinity:** depends on regular configuration and ordered conformations.
 - **Elasticity:** arises from reversible conformational changes.
 - **Thermal behavior:** related to freedom of chain rotation and intermolecular interactions.
 - **Solubility and processability:** influenced by chain flexibility and intermolecular forces.

5. Structural States of Polymers

Depending on temperature and molecular organization, polymers may exist in several **physical states**:

- **Crystalline state:** ordered chain packing; high density, strength, and melting point.
- **Amorphous (glassy) state:** disordered chains; rigid below glass transition temperature (T_g).
- **Rubbery state:** above T_g , chains gain mobility and exhibit elasticity.
- **Viscous flow state:** at high temperatures, chains move freely like in a melt.

Control Questions:

1. What distinguishes the polymer state of matter from low-molecular substances?
2. Define the terms “configuration” and “conformation.”
3. What is the difference between isotactic, syndiotactic, and atactic polymers?
4. Write down all possible configuration isomers for the polybutadiene (polychloroprene) dyad (triad).
5. How can conformation change without altering chemical bonds?
6. How do configuration and conformation affect polymer crystallinity and elasticity?
7. What physical states can polymers exhibit depending on temperature?
8. Why is conformational flexibility important for polymer properties?

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