Lecture 8.

Theme. Flexibility of the polymer chain. Free-jointed chain.

Aim: generate the following learning outcomes:
- describe the mechanism of bending polymer molecules;
- to characterize quantitative criteria for assessing the flexibility of macromolecules;

Purpose:

To understand the factors that determine polymer chain flexibility and the behavior of loosely linked polymer chains, which influence elasticity, entanglement, and mechanical properties of polymers.

Lecture content:

Intramolecular rotation and flexibility of the macromolecule.

Quantitative characteristics of the flexibility of macromolecules (RMS distance between the ends of the chain, radius of inertia of the macromolecule, statistical segment, persistent length).

A free-jointed chain as an idealized model of a flexible macromolecule. The distribution function of the distances between the ends of a freely articulated chain (Gaussian tangles).

The average size of the macromolecule, taking into account the constancy of the valence angles. Energy barriers of internal rotation; the concept of the nature of the braking potential.

Rotary isomers and flexibility of real circuits.

The relationship of flexibility (rigidity) of macromolecules with their chemical structure: factors affecting the flexibility of real chains.

Main Questions:

1. What determines the flexibility of a polymer chain?
2. What is meant by a "loosely linked" polymer chain?
3. How does chain flexibility affect physical and mechanical properties of polymers?
4. What structural features influence flexibility and mobility of polymer chains?
5. How do loosely linked chains contribute to rubbery and amorphous states?

Key Theses:

1. Polymer Chain Flexibility

- **Chain flexibility** refers to the ability of a polymer chain to **change its conformation** due to rotation around single covalent (σ) bonds without breaking the backbone.
- Flexibility depends on **chemical structure, bond types, side groups, and steric hindrance**.

Factors influencing chain flexibility:

1. **Backbone composition:**
   - Chains with single C–C bonds (e.g., polyethylene) are more flexible than those with rigid units (e.g., aromatic rings in polycarbonate).
2. **Side groups:**
   - Large or bulky side groups restrict rotation and reduce flexibility.
   - Small substituents (H, CH_3) allow more rotational freedom.
3. **Chain interactions:**
   - Strong intermolecular interactions (hydrogen bonding, π–π stacking) reduce flexibility.
   - Weak van der Waals interactions allow more mobility.
4. **Temperature:**
   - Above the **glass transition temperature (Tg)**, chains gain rotational freedom and flexibility increases.

2. Loosely Linked Polymer Chains

- **Loosely linked chains** refer to polymer chains that are **not cross-linked or heavily entangled**, allowing them to move and rotate more freely.
- These chains can **uncoil, stretch, and coil** in response to external forces, contributing to **elasticity** and **viscoelastic behavior**.

- They are characteristic of **amorphous and rubbery polymers**, such as natural rubber or lightly cross-linked elastomers.

Features of loosely linked chains:

- High conformational mobility.
- Low entanglement density.
- Ability to form **random coils** in solution or amorphous solids.
- Provide **entropy elasticity**, where polymer chains resist stretching due to an increase in disorder when relaxed.

3. Relationship Between Flexibility and Polymer Properties

- **Elasticity:** Flexible, loosely linked chains can return to their original shape after deformation.
- **Viscosity and flow:** High flexibility enhances chain mobility, leading to lower melt viscosity.
- **Crystallinity:** Excessive flexibility may reduce the ability to form ordered crystalline regions.
- **Mechanical toughness:** Flexible chains dissipate energy efficiently, improving toughness.

Examples:

- **Polyethylene:** flexible linear chains → high ductility.
- **Natural rubber:** loosely linked, flexible chains → excellent elasticity.
- **Polyvinyl chloride (PVC):** bulky side groups → lower flexibility → stiffer material.

4. Applications and Importance

- **Elastomers**: Loosely linked, flexible chains allow repeated stretching and recovery.
- **Fibers**: Chain flexibility affects spinning and orientation.
- **Thermoplastics**: Flexibility determines processability (injection molding, extrusion).
- **Biomedical polymers**: Flexibility is critical for hydrogels and soft tissue implants.

Control Questions:

1. What determines the flexibility of a polymer chain?
2. How do side groups and backbone structure affect chain mobility?
3. Define a loosely linked polymer chain.
4. Why do loosely linked chains contribute to elasticity?
5. List the main quantitative criteria for assessing the flexibility of macromolecules.
6. Name the possible kinetic elements in polymers.
7. Define the concept of a segment of a polymer chain.
8. Explain the concept of thermodynamic flexibility.
9. How does chain flexibility influence crystallinity and mechanical properties?
10. Give examples of polymers with highly flexible chains.
11. What is entropy elasticity and how is it related to chain flexibility?

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