

Lecture 12.

Theme. The nature of polymer solutions, features of their physical and chemical properties. Dissolution thermodynamics

Aim: generate the following learning outcomes:

- to distinguish the main differences in the properties of polymer solutions from the properties of solutions of low molecular weight compounds;
 - explain the concepts of "bad", "good", "ideal" solvent in relation to polymer solutions;
 - formulate the change in thermodynamic functions during the dissolution of polymers;
 - describe the concepts of "second virial coefficient", "Huggins constant", "Flory temperature";
 - remember the basic methods for determining the molecular weight of polymers and the limits of their applicability.
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Purpose:

To understand the **behavior of polymers in solution**, their **unique physical and chemical properties**, and the **thermodynamic principles** governing polymer dissolution.

Lecture content:

Macromolecules in solutions. Unlimited and limited swelling.

The stages of polymer dissolution.

Criteria for polymer dissolution.

The difference between true and colloidal solutions.

The thermodynamics of polymer dissolution.

The viscosity of dilute solutions. Reduced and characteristic viscosity.

The relationship of the characteristic viscosity with the molecular weight and the average size of macromolecules.

Main Questions:

1. What distinguishes polymer solutions from low-molecular-weight solutions?

2. How do polymer molecular weight and chain structure affect solubility?
 3. What are the thermodynamic factors governing polymer dissolution?
 4. How do concentration, temperature, and solvent quality influence polymer solution properties?
 5. What are the key physical and chemical properties of polymer solutions?
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Key Theses:

1. Nature of Polymer Solutions

- A **polymer solution** consists of **long-chain macromolecules dispersed in a solvent**.
- Compared to low-molecular-weight solutes, polymers exhibit **unique solution behavior** due to large size, chain flexibility, and entanglements.

Types of polymer solutions:

1. **True (molecular) solutions:** individual polymer chains are fully solvated and dispersed.
2. **Colloidal solutions:** polymer chains aggregate or form micelle-like structures.
3. **Gels:** highly entangled or cross-linked chains form a semi-solid network with solvent trapped inside.

2. Features of Physical and Chemical Properties

- **Viscosity:** polymer solutions have **high viscosity even at low concentrations** due to chain entanglement and hydrodynamic volume.
- **Osmotic pressure:** very low for polymer solutions compared to molar concentrations of low-molecular-weight solutes; depends on **number of chains, not chain length**.
- **Diffusion:** slow diffusion of macromolecules due to large size and chain entanglements.
- **Chemical reactivity:** functional groups along polymer chains may interact with solvent or other solutes, affecting solution behavior.
- **Non-ideal behavior:** polymer solutions often **deviate from Raoult's law** due to size asymmetry and chain interactions.

3. Dissolution Thermodynamics

- **Polymer dissolution** is a thermodynamically controlled process.

Key points:

1. **Entropy of mixing** is relatively small for polymers because fewer macromolecules contribute to disorder compared to many small solvent molecules.
2. **Enthalpy of mixing** \ depends on **polymer-solvent interactions**:
 - Good solvent: favorable interactions → polymer dissolves.
 - Poor solvent: unfavorable interactions → polymer precipitates.
3. **Flory-Huggins theory** is commonly used to describe polymer solution thermodynamics, accounting for chain length and solvent-polymer interactions.

Factors affecting dissolution:

- Polymer molecular weight: higher molecular weight → lower solubility.
- Solvent quality: polar vs. non-polar interactions.
- Concentration: at high concentration, entanglements and viscosity limit dissolution.

4. Summary of Polymer Solution Behavior

- Polymer solutions are **viscoelastic**: they exhibit both viscous and elastic responses.
- Chain entanglements strongly influence **flow, diffusion, and mechanical properties** of solutions.
- Thermodynamics of dissolution determines **solubility limits, miscibility, and phase separation**.
- Understanding polymer solutions is essential for **coatings, adhesives, biomedical applications, and polymer processing**.

Control Questions:

1. What distinguishes polymer solutions from low-molecular-weight solute solutions?
2. List the main features of the properties of polymer solutions.
3. Name and describe the types of polymer solutions.
4. How does polymer molecular weight affect solubility?
5. Explain why polymer solutions often have high viscosity.
6. What is the thermodynamic condition for polymer dissolution?
7. How does solvent quality affect polymer solubility?
8. Name the main cause of endothermic dissolving of flexible-chain polymers.
9. Define the concepts of "good", "bad" and ideal solvent for polymers.

10. What role does the Flory-Huggins parameter play in polymer solution behavior?
 11. Explain the physical meaning of the Huggins constant.
 12. Name the methods for determining the second virial coefficient.
 13. Name four possible options for reducing the free energy of the system when the polymer dissolves.
 14. Give examples of practical applications of polymer solutions.
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14. <http://www.hemi.nsu.ru/>