Lecture 15.

Theme. Chemical reactions of polymers, features.

Aim: generate the following learning outcomes:

- the main differences between reactions on polymers from similar reactions of low molecular weight substances;
- - main effects of polymeranalogical reactions;

Purpose:

To understand the **types of chemical reactions that polymers undergo**, their **mechanisms**, and the **specific features** that distinguish polymer reactions from low-molecular-weight compounds.

Lecture content:

Features of reactivity of functional groups of macromolecules.

The influence of the local environment of the functional group, the configuration characteristics and conformation of the chain, the supramolecular organization of polymers on the reactivity of macromolecules.

Chemical reactions that do not lead to a change in the degree of polymerization of macromolecules: polymeranalogical transformations and intramolecular transformations.

Examples of the use of polymeranalogical transformations and intramolecular reactions for the production of new polymers.

Main Questions:

- 1. What are the main types of chemical reactions of polymers?
- 2. How does the polymer structure affect chemical reactivity?
- 3. What are the key features of chemical reactions in polymers compared to small molecules?

- 4. How do reaction conditions (temperature, solvent, catalysts) influence polymer reactions?
- 5. What practical applications rely on chemical reactions of polymers?

Key Theses:

1. Types of Chemical Reactions of Polymers

- **Substitution reactions:** replacement of functional groups on the polymer chain.
 - Example: Halogenation of polyethylene.
- Addition reactions: addition of small molecules to unsaturated polymer chains.
 - o Example: Hydrogenation of polybutadiene.
- Elimination reactions: removal of small molecules from polymer chains, often forming double bonds.
 - Example: Dehydrohalogenation of PVC.
- Cross-linking reactions: formation of covalent bonds between polymer chains.
 - o Example: Vulcanization of rubber.
- **Degradation reactions:** cleavage of polymer chains by heat, light, or chemicals.
 - o Example: Thermal or oxidative degradation.

2. Features of Polymer Reactions

- **Reactivity depends on chain structure:** functional groups, backbone type, degree of crystallinity.
- **Steric hindrance:** bulky polymer chains reduce reaction rates compared to small molecules.
- **Diffusion-limited reactions:** for solid or semi-solid polymers, reagents must diffuse into the polymer matrix.
- **Heterogeneity:** reactions may occur differently in amorphous vs crystalline regions.
- **Macromolecular stability:** high molecular weight can limit volatility of products and intermediates.

3. Thermodynamic and Kinetic Considerations

- **Activation energy:** reactions often require higher temperatures due to reduced mobility.
- Reaction rate: influenced by chain mobility, solvent, temperature, and catalysts.
- **Degree of conversion:** partial reaction may change polymer properties without full chemical transformation.

4. Practical Applications

- Functionalization of polymers: introduces reactive groups for adhesives, coatings, or biomedical applications.
- Cross-linking for mechanical strength: vulcanization of rubber, epoxy curing.
- **Polymer degradation and recycling:** controlled chemical breakdown for reuse or disposal.
- **Surface modification:** plasma or chemical treatments to alter surface properties.

Control Questions:

- 1. List the main types of chemical reactions of polymers with examples.
- 2. List the effects known to you that can be detected in chemical reactions of polymer functional groups.
- 3. How does polymer structure influence chemical reactivity?
- 4. Why are polymer reactions often slower than reactions of small molecules?
- 5. How do amorphous and crystalline regions affect polymer reactions?
- 6. Explain the role of cross-linking in polymer chemistry.
- 7. What are the main practical applications of chemical reactions of polymers?

References for lecture content:

- 1. Introduction to Polymer Science and Chemistry: A Problem-Solving Approach, Second Edition 2nd Edition / by Manas Chanda, CRC Press; 2nd edition (January 11, 2013)
- 2. Polymer Chemistry 2nd Edition / by Paul C. Hiemenz, Timothy P. Lodge, CRC Press; 2nd edition (February 15, 2007)

- 3. Семчиков Ю.Д. Высокомолекулярные соединения: Учебник для вузов. М.:Академия, 2003, 368 .
- 4. Киреев В.В. Высокомолекулярные соединения. Учебник. М.: -Юрайт.- 2015.-602 с.
- 5. Зезин А.Б. Высокомолекулярные соединения. Учебник и практикум. М.: -Юрайт.-2017. 340 с.
- 6. В.Н.Кулезнев, В.А.Шершнев. Химия и физика полимеров. М.: Колос C, 2007.- 366с.
- 7. Тугов И.И., Кострыкина. Химия и физика полимеров. –М: Химия,1989. 430c.
- 8. Ергожин Е.Е., Құрманәлиев М.Қ. Жоғары молекулалық қосылыстар химиясы. Алматы, 2008, 407 б.
- 9. Абдықалыкова Р.А. Полимерлерді хим. түрлендіру ж/е модиф. //Оқу құр. -Қазақ унив.-2003.-44 б.
- 10. Абдықалыкова Р.А., Рахметуллаева Р.К., Үркімбаева П.И. Оқу құралы. Алматы, «Қазақ университеті», 2011. -177 бет
- 11. Қаржаубаева Р.Ғ. Полимерлеу процестерінің химиясы //Оқу құр. -Қазақ унив.-2002, 80б.

Internet resources:

- 12. http://www.pslc.ws/index.htm
- 13. http://www.xumuk.ru/
- 14. http://www.hemi.nsu.ru/