MINISTRY OF HIGHER EDUCATION, SCIENCE AND INNOVATION OF THE REPUBLIC OF UZBEKISTAN

NAMANGAN STATE UNIVERSITY

Department of Organic Chemistry

EDUCATIONAL AND METHODOLOGICAL COMPLEX

by subject

CHEMISTRY OF HIGH MOLECULAR COMPOUNDS

Area of Knowledge:	100000-natural subjects
Area of Education:	140000-Physical and natural subjects
Bachelor Directions:	60530100-Chemistry (daytime)

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Content

TEXT OF LECTURES

V semester

Lecture 1

Introduction. Basic concept and characteristics.

Plan

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2. Macromolecule and its chemical link. Degree of polymerization and chain length.
3. The role of polymers in wildlife and their importance as a chemical material.
4. The merits of Uzbek scientists in the development of the science of polymer chemistry.

Reference terms:low molecular weight compounds, high molecular weight compounds, polymers, oligomers, macromolecules, monomeric bond, degree of polymerization, chain length.

1. Basic concept, macromolecular compounds, oligomers, polymers.

Polymers- chemical compounds with a high mol. mass (from several thousand to many millions), whose molecules (macromolecules) consist of a large number of repeating groups (monomeric units). The atoms that make up the macromolecules are connected to each other by the forces of the main and (or) coordination valences.

Some properties of polymers, such as solubility, viscous flow, stability, are very sensitive to the action of small amounts of impurities or additives that react with macromolecules. So, in order to turn a linear polymer from soluble to completely insoluble, it is enough to form 1-2 cross-links per macromolecule.

The most important characteristics of polymers are chemical composition, molecular weight and molecular weight distribution, degree of branching and flexibility of macromolecules, stereoregularity, and others. The properties of polymers essentially depend on these characteristics.

Until recently, solutions of macromolecular compounds (HMCs) were incorrectly referred to as sols. Numerous studies of the properties of HMS solutions have shown that these systems differ in many properties from sols and have a number of specific features.

Many macromolecular compounds (HMCs) are polymers with a molecular weight > 104. Polymer molecules consist of a large number of monomeric units - repeating identical groups of atoms. Structural units of HMC are macromolecules (104-106 g/mol). The size of macromolecules is very large compared to the size of ordinary molecules. For example, if the length of an ethane molecule is several angstroms, then the length of some linear macromolecules is 4000-8000 Å (with a transverse dimension of 3-7.5 Å). Threads with a length of 800 to 1600 mm and a diameter of 1 mm can serve as a model for such molecules.

The structural chemical basis of organisms are natural high-molecular biopolymers: proteins, nucleic acids, polysaccharides, pectins, natural rubber. Natural HWCs are characterized by a constant molecular weight.

Synthetic polymers are obtained as a result of a polymerization or polycondensation reaction. These include: polyethylene, synthetic rubber, phenol-formaldehyde resins. Synthetic polymers are composed of a mixture of macromolecules that vary in length and mass. Thus, HWCs are ordinary organic substances, the molecules of which are very large.

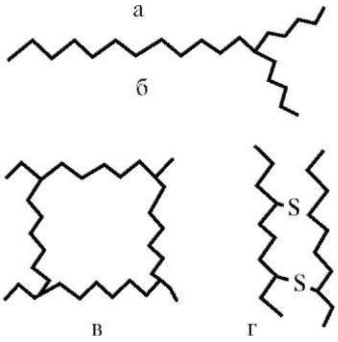
2. Macromolecule and its chemical unit

Almost all important properties of HWCs are closely related to their structure. There are three types of chain structure: linear, branched and spatial (mesh) (Fig. 1).

Linear HWCs are an open linear chain (natural rubber, cellulose).

Macromolecules of branched HWCs are in the form of a linear chain with branches (amylopectin, glycogen).

Spatial (network) HWCs, the macromolecules of which are three-dimensional networks, are formed by segments of a chain structure (for example, phenol-formaldehyde resins). Of the three-dimensional polymers, polymers with a cross-linked structure are distinguished into a special group, the chains of which are cross-linked by short bridges.



Rice. 1 −Schemes of the structure of macromolecules of polymers: a - linear; b - branched; c - spatial; g - stitched

However, of all the structures, it is the linear shape of macromolecules that determines the typical properties of polymers: rubbery elasticity, the ability to form strong films and threads, swell, and give viscous solutions upon dissolution. These properties of chain macromolecules and their solutions are of the greatest interest. Polymers with a spatial structure are not able to dissolve, therefore, we do not consider the properties of network polymers.

The main historical stages of the development of the Navy

Natural HWCs have been known for a very long time. Natural materials such as various fibers, leather and rubber have been used since ancient times. Naval chemistry as an independent science began to develop only in the 1920s.

The term “polymeria” was introduced into science by I. Berzelius in 1833 to denote a special type of isomerism, in which substances (polymers) having the same composition have different molecular weights, for example, ethylene and butylene, oxygen and ozone. This content of the term did not correspond to modern ideas about polymers. “True” synthetic polymers were not yet known at that time.

A number of polymers were apparently obtained as early as the first half of the 19th century. However, chemists then usually tried to suppress polymerization and polycondensation, which led to the “tarring” of the products of the main chemical reaction, i.e., in fact, to the formation of polymers (until now, polymers are often called “resins”). The first references to synthetic polymers date back to 1838 (polyvinylidene chloride) and 1839 (polystyrene),

The chemistry of polymers arose only in connection with the creation of the theory of chemical structure by A.M. Butlerov. A.M. Butlerov studied the relationship between the structure and relative stability of molecules, which manifests itself in polymerization reactions. The science of polymers was further developed mainly due to the intensive search for ways to synthesize rubber, in which the largest scientists from many countries participated (G. Bouchard, W. Tilden, German scientist K Garries, I. L. Kondakov, S. V. Lebedev and others). In the 1930s, the existence of free radical and ionic mechanisms of polymerization was proved. The works of W. Carothers played an important role in the development of ideas about polycondensation.

Since the early 1920s, theoretical concepts of the structure of polymers have also been developed. Initially, it was assumed that such biopolymers as cellulose, starch, rubber, proteins, as well as some synthetic polymers similar in properties to them (for example, polyisoprene), consist of small molecules that have an unusual ability to associate in solution into complexes of a colloidal nature due to their non covalent bonds (the theory of “small blocks”). The author of a fundamentally new idea of polymers as substances consisting of macromolecules, particles of unusually large molecular weight, was G. Staudinger. The victory of the ideas of this scientist forced us to consider polymers as a qualitatively new object of study in chemistry and physics.

Determining the structure of HMS and describing their properties for a long time was hampered by the impossibility of isolating them by methods of classical organic chemistry in a chemically pure state and finding their exact physical constants (melting temperature, boiling point, molecular weight). The study of the structure and properties of HWCs became possible only with the development of physical chemistry and the advent of such research methods as X-ray diffraction, electron diffraction, etc. Special methods for determining molecules were also created. masses, shapes and structures of giant molecules unknown in classical chemistry.

The first attempts to describe the properties of HMS based on the concepts of classical chemistry led to the colloidal theory of the structure of HMS, since some features of HMS solutions were close to the well-known colloidal systems at that time.

The micellar theory of K. Meyer and G. Mark, and especially the macromolecular theory of G. Staudinger, had the greatest significance for the subsequent development of the chemistry of HMS.

According to the micellar theory of structure, HWCs are built from micelles, which are bundles of rigid macromolecules. Each micelle, which forms a surface-organic structural unit, includes 40-60 parallel macromolecules of the polymer. The behavior of these structural units determines all St. Islands of the Navy.

Staudinger, observing the very high viscosity of even low-concentration HMS solutions, suggested the existence of very long, unassociated molecules, the dimensions of which determine all the features of HMS. Staudinger showed that the higher and lower members of the polymer homologous series are constructed in the same way and the different ability to swell, dissolve, and other physical chemical properties are due to the difference in molecular weights.

Staudinger denied the possibility of association of molecules not only in dilute, but also in concentrated solutions of polymers. He believed that polymer molecules are rigid sticks that cannot noticeably change their shape.

Staudinger's theory had many shortcomings. But despite this, she had a progressive role. This theory for the first time gave the idea of polymers as substances, the size of the molecules of which differs by several orders of magnitude from the size of the NMS molecules, which leads to sharp qualitative differences in the properties of the compounds of these two classes.

The synthesis of a number of polymers was of decisive importance in the creation of a modern theory of the structure of HMS. The powerful development of organic synthesis, which began at the end of the 19th century, and the production of a huge amount of synthetic products, including monomers, served as an impetus for the synthesis of various HWCs.

Thanks to the use of new research methods, it was shown that natural synthetic polymers consist of long filamentous molecules, the molecular weight of which reaches tens and hundreds of thousands.

Based on the results of further studies of the structure of the HWC and their physical properties, modern ideas about the structure of the HWC were formed. According to them, HWCs are built from long, flexible, filamentous molecules that can change their shape. The connection between macromolecules is carried out by the physical forces of intermolecular interaction. All polymers are heterogeneous in physical structure, which is due to the large size and flexibility of macromolecules. Crystallizing polymers are two-phase and have crystalline and amorphous regions. Amorphous polymers are single-phase, but these polymers also have regions of order. Due to the flexibility of macromolecules and their ability to change their shape, polymers have high reversible deformations, which distinguishes them from NMS.

Thermodynamic studies of the properties of polymer solutions carried out by M. Huggins, P. Flory, V.A. Kargin, S.M. Lipatov and other researchers showed that the majority of HWCs form true solutions and only some of them can also form colloidal solutions.

Based on the developed N.N. Semenov of the theory of chain reactions developed the theory of chain polymerization. The creation of the foundations of the theory of polymerization was played by S.V. Lebedev. Using the kinetic method of studying the polymerization process, he was the first to establish the dependence of the polymerization rate on the chemical structure of the initial NMS.

The fundamentals of the theory of polycondensation were developed by W. Carothers, Marvel, G.S. Petrov and A.A. Vanshteidt.

A significant event in the chemistry of polymers was the discovery by K. Ziegler and J. Natta of a method for the synthesis of a new type of HWCs - stereoregular polymers, characterized by a regular structure and extremely high physical and mechanical properties. Great progress has been made in the field of polymer synthesis in the solid phase, as well as the creation of heat-resistant polymer materials and polymers with a system of conjugated bonds.

The role of polymers in wildlife and their importance as industrial materials.

Organic VSM are the basis of living nature. The most important compounds that make up plants are polysaccharides (cellulose, starch), lignin, proteins, pectin substances - HWCs.

There is so much plant mass on earth that the number of HWCs contained in it is expressed in a colossal figure and exceeds the total number of all other org. connections. In the world of plants, the biochemical synthesis of higher polysaccharides and lignin is carried out. The catalysts for complex processes leading to the synthesis of HMC in plants are enzyme proteins, the feedstock in the synthesis of carbohydrates is CO2, which is the final product of the oxidation of any carbon-containing compounds, is continuously released into the atmosphere. In this way, the carbon cycle is maintained and its balance is maintained on earth.

The basis of the animal world is also made up of HWCs - proteins, which are the main component of almost all substances of animal origin. Muscles, connective tissues, brain, blood, skin, hair, wool are made up of HWCs. For the needs of mankind, various materials of animal origin are widely used - food products (meat, fish, milk), wool, natural silk and leather, the main part of which are proteins. Nucleic acids play an exceptional role in the life of animals and plants. They take part in the biochemical synthesis of proteins.

Mixed HWCs are widespread in the animal and plant kingdoms. These are proteins that simultaneously contain a carbohydrate or lipid component or are associated with nucleic acids, and polysaccharides containing protein or lipid, or both components. Mixed HWCs perform extremely important functions in the body. They determine the group affiliation of the human and animal organisms and the specificity of microbes, playing an important role in the phenomenon of immunity. Mixed HWCs are part of the nervous and connective tissues of the body, secretory fluids, and are involved in the regulation of nervous processes.

Of the other natural HWCs, natural rubber is the most important, although its role is limited only to technical applications.

The main part of the earth's crust consists of oxides of silicon, aluminum, and other multivalent elements combined into macromolecules. Silicic anhydride [SiO2]n, it is contained in the earth's crust in the form of a polymer of pure silicic anhydride and HM complex silicates (aluminum silicates). The most common modification of silicic anhydride is quartz. Rock crystal and amethyst are also nearly pure polymeric silicic anhydride. Polymeric aluminum oxide [Al2O3]n is found in the form of the mineral corundum and the precious minerals ruby and sapphire. Clay in-va consist of HM aluminosilicates of variable composition. Mica and asbestos are silicates of complex variable composition. HWCs are and occur in nature various modifications of carbon - diamond, graphite, amorphous carbon.

3. The merits of Uzbek scientists in the development of the science of polymer chemistry.

Chemistry and physics of cotton cellulose by Uzbek polymer chemists, radiation chemistry of polymers (academician Usmanov Kh.U., professors Tillaev R.S., Tashmukhamedov S.O., Azizov Yu.A., Rozikov K.Kh., Aikhodzhaev B.I. ., Rakhmonberdiev G. et al.), Fluoropolymers (prof. Yulchiboev). (of particular importance are fundamental research in the field) and medical polymers (Prof. Musaev O.N., Academician Rashidova S.Sh., Prof. Nadzhmiddinov Sh., Prof. Turaev A.S., etc.). This study is associated with the name of the scientist who began the study of polymer chemistry in Uzbekistan - Honored Worker of Science and Technology of Uzbekistan, Academician Kh.U. Usmanov.

Uzbekistan is one of the leading cotton growing countries and has innumerable reserves of natural polymer - cellulose. In addition, the abundance of pentose-containing raw materials and the availability of natural gas required the creation of a large center for chemistry and polymer technology in Uzbekistan.

Chemistry of natural polymers, started in 1950 at the Institute of Chemistry of the Academy of Sciences of the Republic of Uzbekistan with the study of thermodynamic, physicochemical and mechanical properties of cotton cellulose and esters.

laboratory was established. This can be considered the period of the emergence of polymer science in Uzbekistan. The first works on polymers, as well as the creation of institutes and laboratories in this field, are associated with the name of G.U. Usmanov, Academician V.A. Kargin.

The Laboratory of Chemistry of Natural Polymers has developed studies of cellulose biosynthesis, its structure, physicochemical, thermodynamic and other properties.

Copolymers of acrylonitrile with vinyl acetate, styrene, methyl methacrylate, vinylpyrrolidone, and acrylic acid esters have been synthesized, and their activity in copolymerization reactions with acrylonitrile has been studied. When studying the synthesis and properties of synthetic polymers, Acad. Services M.A. Askarova are wonderful.

Acad. Akhmedov K.S. Under his leadership, water-soluble polyelectrolytes and surfactants were developed and put into practice in order to direct the physical and chemical properties of disperse systems in the desired direction.

In 1960, at the Faculty of Chemistry of the National University of Uzbekistan named after Mirzo Ulugbek, complex research began in the field of radiation modification of synthetic polymers and new methods for obtaining thermo-chemo- and light-resistant fluoropolymers were developed.

The university was the first in Central Asia to study the chemistry and physical chemistry of physiologically active polymers. In this area, Professor O.N. Musaev and his students synthesized a number of new water-soluble polymers with pharmacological activity based on alkaloids and drugs. In recent years, at the Institute of Polymer Chemistry and Physics of the Academy of Sciences of the Republic of Uzbekistan under the guidance of Academician S.Sh. Rashidova synthesized and studied polymers with specific properties, which makes a worthy contribution to the development of this area.

Lecture 2

Classification of polymers.

Plan:

1. Classification of polymers depending on the appearance
2. Chemical composition, main chain, link.
3. Linear, branched and cross-linked polymers
4. Organic and inorganic polymers.

Reference terms:structure, polysaccharides, synthetic polymer, artificial polymer, natural polymer, elastomer, plastomer, fiber, homochain polymers, heterochain polymers, carbon chain polymers, nomenclature.

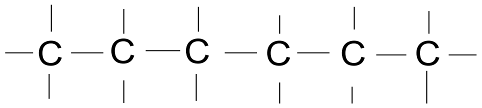
1. Classification of polymers depending on the appearance

Macromolecular compounds can be natural or synthetic. The natural ones include proteins, polysaccharides, natural resins, natural rubber and, and the synthetic ones include polyethylene, polystyrene, polyamides, phenolic resins. High-molecular compounds consist of large molecules, the molecular weight of which exceeds several thousand, and sometimes can reach many millions. The molecules of such compounds consist of a combination of small molecules of the same or different chemical structure. By connecting with each other by the forces of the main valences (chemical bonds), small molecules form a high-molecular substance.

In most cases, macromolecular compounds are polymers - substances whose molecules consist of many timesrepeating structural units. One polymer molecule can include one, two, and sometimes three or more repeating structural units. The wide interest in polymers, the numerous scientific papers devoted to them, and the large volume of industrial production of synthetic polymers are primarily due to the unique complex of their physical and mechanical properties. The most important physical properties of polymers are determined by their chemical structure. At first glance, it seems that many properties, especially those of crystalline polymers, are mainly determined by their structure. However, in fact, one or another type of supramolecular organization (with all its diversity) ultimately depends on the chemical structure of the polymer chain.

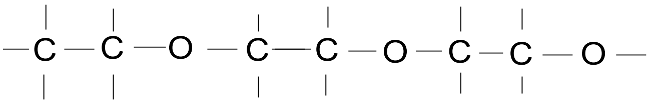
2. Chemical composition, main chain, link.

The main chain consists of the same atoms as carbon, sulfur, phosphorus, and so on. homozygous polymers. Carbon chain polymers are polymers in which the main chain of the macromolecule consists of only carbon atoms:



$$-C-C-C-C-C-C-$$

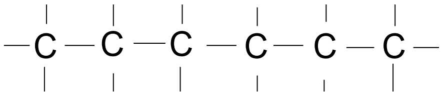
Heterochain polymers are polymers in which the main chain consists of different atoms:



$$-C-C-O-C-C-O-C-C-O-$$

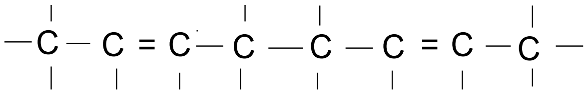
Carbo-chain polymers are divided into two groups:

1) The monomer chain link of saturated carbon chain polymers consists of carbon-carbon bonds.



$$-C-C-C-C-C-C-$$

2) The chain of unsaturated carbonaceous polymers has a double bond in the monomer chain.



$$-C-C=C-C-C-C=C-C-$$

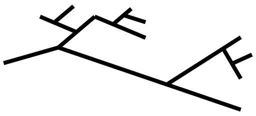
3. Linear, branched and cross-linked polymers

Polymers are compounds in which a large number of identical or unequal atomic groups alternate more or less regularly, connected by chemical bonds into long linear chains or chains with side branches, as well as into spatial networks. Depending on the composition, organic, inorganic and organoelement polymers are distinguished. Organic compounds of this class have been studied most fully, and therefore it is expedient to consider the main regularities of the structure of polymers using their example.

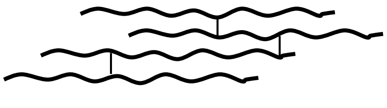
Linear polymers are polymers whose macromolecules are long chains with a very high degree of asymmetry. If in general terms the remainder of the monomer is denoted by the letter A, then the formula of a linear polymer can be schematically written as follows:

$$\cdots—A—A—A—A—A—A—\cdots$$

A branched polymer is a long chain (usually called the main, or main) with side branches (side chains), and the number of these branches and their length can vary within very wide limits.



-branched structure



-shielded structure

4. Organic and inorganic polymers.

The simplest organic polymer is polyethylene, a polymerization product of ethylene. Ethylene is an unsaturated hydrocarbon that easily enters into addition reactions. Two ethylene molecules combine to form a butylene molecule:

$$\mathbf{CH2{=}CH2{+}CH2{=}CH2 \rightarrow CH3\text{-}CH2\text{-}CH{=}CH2}$$

The starting material, ethylene, is called a monomer, and the resulting butylene is called a dimer. Three ethylene molecules combine to form a trimer, four to form a tetramer, and so on. If n molecules of a monomer are combined, a polymer is formed (from the word "poly" - a lot):

$$nCH_2{=}CH_2 \longrightarrow \left[-CH_2-CH_2- \right]_n$$

Repeatedly repeating groupings, which are residues of monomers, are called links, or monomeric links; a large molecule composed of units is called a macromolecule or polymer chain. The number of links in the chain is called the degree of polymerization and is denoted by the letters n or P. The product of the degree of polymerization n and the molecular weight of the link Mzv is equal to the molecular weight of the polymer: Mpol \u003d nMzv. The degree of polymerization can vary widely: from n equal to several units to n equal to 5000-10000 and even more. Polymers with a high degree of polymerization are called high polymers, polymers with a low degree of polymerization are called oligomers. A macromolecule can be built from chemically identical monomers or from monomers of different structures. Polymers built from the same monomers are called homopolymers. Polymer compounds whose chains contain several types of monomer units are called copolymers or mixed polymers. Residues of monomers can combine in a macromolecule with each other to form polymers of a linear, branched, or network (spatial) structure.

Polymers are classified according to several parameters:

Origin

- natural (existing in nature): cellulose, starch, chitin, proteins, nucleic acids, etc.
- synthetic polymers (not existing in nature, synthesized): polyethylene, polypropylene, etc.
- artificial (modifications of natural polymers obtained synthetically): nitrocellulose, benzylcellulose, methylcellulose, cellulose acetate, etc.

By application

- plastics and organic glasses
- synthetic rubbers

If Tst>Troom, then the polymer is classified as a plastic (styrene, PVC, polymethyl methacrylate, etc.)

If Tst<Troom, then the polymer is classified as synthetic rubber (SR), where Tst is the glass transition temperature, Troom is room temperature

- synthetic and artificial fibers
- films and numerous decorative and protective coatings (varnishes, paints, enamels)
- biomedical materials.

By the presence in the macromolecule of one or more types of monomer units

- homopolymers, consisting of monomer units of the same type;

- copolymers, consisting of several different types of monomer units (binary copolymers, terpolymers, multicomponent copolymers).

Lecture 3
Chemical classification of polymers
Plan:

1. Polymers and copolymers of monoolefins and their derivatives.
2. Polyesters. Polyacetals.
3. Polyamides, polyurethanes, polysaccharides, proteins, nucleic acids.
4. Polysiloxanes

Classification is carried out according to the type of atoms included in the chain:

- organic polymer(the composition includes organogenic elements - C, N, O, P, S). They are divided into homochain (the main chain contains only carbon atoms) and heterochain (the main chain includes other atoms). This class of polymers includes biopolymers.
- organoelement polymers(in the composition of the main chain, along with carbon atoms, there are atoms of Si, Al, Ti, Ge, B).
- inorganic polymers (the main chain does not contain carbon atoms, such as silicones).

The heterogeneity of the polymer in chemical composition lies in the fact that the same chain contains units of different composition. Chemical heterogeneity is observed in all industrial images of cellulose ethers, polyvinyl alcohol and some other polymers. The chemical composition of such polymers is usually characterized by the average percentage of functional groups present in them (for example, acetyl groups) or nitrogen content, and so on.

As already noted, a characteristic feature of polymer compounds is a high molecular weight. However, there are no polymers in which all molecules would have exactly the same size, or in other words, the same degree of polymerization. Along with very large molecules in a polymer, there can be small (with a molecular weight of 1000) and molecules of intermediate sizes. Consequently, any polymer is more or less heterogeneous in molecular weight, or, as they say, polymolecular ("polydisperse"). Therefore, in polymer chemistry, the concept of average molecular weight is used.

A number of polymeric compounds of the same chemical structure, differing only in molecular weight - a polymer homologous series.

Polymeric hydrocarbons are non-polar. These include: polyethylene, polypropylene, polybutadiene, polyisoprene. The most polar polymers are polyvinyl alcohol, cellulose, starch containing a large number of polar OH groups, polyacrylonitrile in which there are a large number of highly polar CN groups, polyacrylic and polymethacrylic acids (COOH groups). Polyvinyl chloride containing C-Cl bonds and cellulose acetate (OCOSH3 groups) occupy an intermediate position in polarity. Even less polar are polymeric esters (for example, polyacrylates and polymethacrylates). However, the presence of polar groups in a molecule does not always indicate the polarity of molecules as a whole. If the polar bonds in the molecule are arranged symmetrically, then their electric fields are compensated, and the dipole moment in the molecule is zero.

Polysaccharides are biopolymers whose molecules consist of monosaccharide residues linked by glycosidic bonds.

classificationpolysaccharides are carried out:

1)according to the functions that polysaccharides perform in the body: there are structural and reserve polysaccharides;

2)according to the composition of monomer units: homopolysaccharides and heteropolysaccharides are distinguished.

Homopolysaccharidesare characterized by the presence in the molecule of only one type of monosaccharide as a monomeric link, although the types of bonds of the glycosidic bond between the links may be different.

Heteropolysaccharidescharacterized by the presence of two or more types of monomer units.

3)Unlike other classes of biopolymers, polysaccharides can exist both in the form of linear and branched structures.

4)The molecular weights of polysaccharides range from several thousand to several million daltons and can only be determined approximately.

Cellulose- the most common plant structural polysaccharide in nature. It has great mechanical strength and acts as a supporting material for plants.

Lecture 4

The concept of molecular weight characteristics of polymers

Plan

1. Molecular weight of polymers,
2. Molecular weight distribution and the concept of average molecular weight.
3. Fractionation methods.

Reference terms:Average molecular weight, polymer homologues, polydispersity.

1. Molecular weight of polymers, molecular weight distribution and the concept of average molecular weight.

The molecular weight, which is one of the main characteristics of any chemical compound, acquires a special role in the case of high-molecular compounds, since it also serves as a measure of the length of a chain molecule. The latter is also characterized by the number of repeating units or the degree of polymerization of the macromolecule (P), which is related to the molecular weight (M) by a simple ratio:

$$\mathbf{M = Pm}$$

where m is the molecular weight of the unit.

The concepts of the molecular weight of a polymer and a low molecular weight compound are not adequate to each other. This difference is due to the fact that almost all synthetic polymers, even extremely purified ones, are not individual compounds in the generally accepted sense, but are a mixture of polymer homologues of the same composition but different degrees of polymerization, i.e. different molecular weights (i.e. polymolecularity). (Unlike synthetic polymers, biopolymers are individual compounds, all molecules of which have exactly the same molecular weight). In fact, for polymers, in contrast to low molecular weight compounds, the law of composition constancy is not fulfilled. Violation of the law of composition constancy for polymers is also due to the fact that the terminal units of macromolecules differ from the main, repeating units of the chain. During polymerization, violations of the main chain structure are possible due to lateral branches of various lengths. The contribution of the last two reasons in comparison with the first - polydispersity, in violation of the law of composition constancy for polymers is negligible.

Note that the concepts of molecular weight and macromolecule, in general, lose their meaning for cross-linked polymers with a spatial, three-dimensional structure. Such polymers are characterized by the density (or frequency) of crosslinking, that is, the length of the chain segments between the nodes of the three-dimensional grid.

Polymolecularity or polydispersity of synthetic macromolecular compounds is due to the special nature of the reactions of their preparation. For a complete molecular weight characterization of polymers, it is necessary to know their molecular weight distribution function (MWD). There are differential and integral MWD functions, in turn, each of them can be numerical or mass, depending on whether the numerical or mass fraction of macromolecules is used.

It is clear that these two methods of averaging are not equivalent. Indeed, suppose that two different fractions contain the same number of molecules. Then the numerical fractions of these fractions will coincide with each other, and their mass fractions will differ in accordance with the molecular weights of these fractions.

By definition, the differential numerical function of MWD - qn (M) is equal to the ratio of the numerical fraction of macromolecules (dn), having a molecular weight in the range from M to M + dM, to the value of this interval (dM), i.e. qn(M) = dn/dM; similarly, the differential mass function of the MWD - qw(M) is determined by the relation

qw(M) = dw/dM, where dw is the mass fraction of macromolecules with a molecular weight ranging from M to M + dM.

The normalization conditions require that

$$\int_0^\infty \rho(M)dM = 1$$

or, if we assume that M varies discretely,

$$\sum_i \rho_i(M) = 1.$$

In addition to the differential functions of MWD, integral (numerical or mass) functions are used that determine the corresponding total fraction of all macromolecules with a mass $\leq M$,those.

$$q_n(M) = \int_0^M \rho_n(M)dM \text{ And } q_w(M) = \int_0^M \rho_w(M)dM$$

On fig. Figures 3a and 3b show numerical differential and integral functions of the MMP as an example.

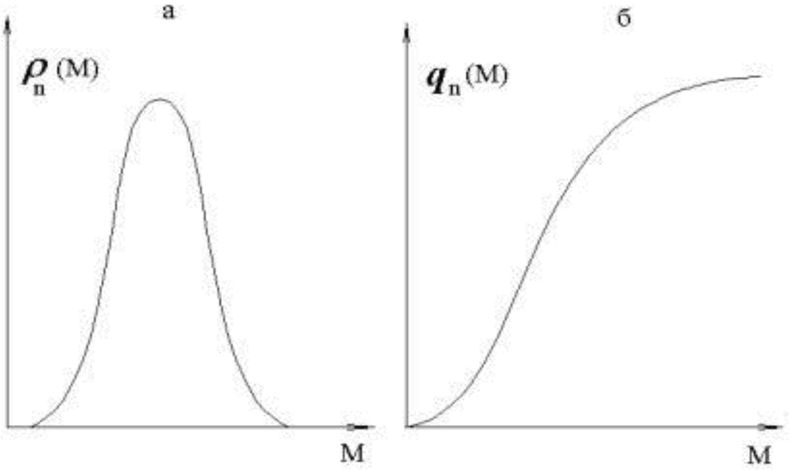


Fig.3. Numerical differential qn(M) (a) and integral qn(M) (b) functions of the MMP.

It should be noted that any of the four indicated functions completely describes the MWD of the polymer, all of them are interconnected and can be recalculated one from the other. However, in practice, due to the experimental complexity of determining the MWD functions, average molecular weights are used much more often. The latter can be determined experimentally by various physicochemical methods: osmometric method, light scattering method, high-speed sedimentation, viscometry, etc.

The polydispersity of polymers and different methods of averaging lead to different average mass characteristics of macromolecules. Thus, averaging "over the number" and "over the mass" leads to the average number $(\overline{M}_n)$ and medium-mass $(\overline{M}_w)$ molecular weights, which by definition are:

$$\overline{M}_n = \int_0^\infty M \rho_n(M)dM, \quad \overline{M}_w = \int_0^\infty M \rho_w(M) dM$$

Express $\overline{M}_w$ through the numerical function of MWD - qn(M), for this we determine the mass fraction dw of a certain fraction; while taking into account that it is equal to the number of all chains from M to M + dM, multiplied by their mass and divided by the mass of the entire sample:

Then for the mass function qw(M) we get:

$$\rho_w(M) = \frac{dw}{dM} = \frac{M}{\overline{M}_n}\rho_n(M)$$

and finally:

$$\overline{M}_w = \int_0^\infty \frac{M^2}{\overline{M}_n}\rho_n(M)dM = \frac{\int_0^\infty M^2\rho_n(M)dM}{\int_0^\infty M\rho_n(M)dM}$$

In some cases, the so-called “z-average” molecular weight is used, which from the definition is equal to:

$$\overline{M}_z = \frac{\int_0^\infty M^3 \rho_n(M)dM}{\int_0^\infty M^2 \rho_n(M)dM}$$

From the above definitions it is not difficult to understand the physical meaning $\overline{M}_n$ And $\overline{M}_w$, whereas $\overline{M}_z$- has no direct physical meaning. At the same time, all average molecular weights are associated with the so-called MWD moments.

If we take into account that the MWD functions are actually discrete, and not continuous, and move from integration to summation over M, then the number average and mass average molecular weights will be expressed as:

$$\overline{M}_n = \frac{\sum_1^\infty M_i \rho_i}{\sum_1^\infty \rho_i} = \sum_1^\infty n_i M_i \quad \text{And} \quad \overline{M}_w = \frac{\sum_1^\infty M_i^2 \rho_i}{\sum_1^\infty M_i \rho_i} = \sum_1^\infty M_i \frac{M_i \rho_i}{\sum_1^\infty M_i \rho_i} = \sum_1^\infty M_i w_i$$

where ni and wi are the numerical and mass fractions of a macromolecule of mass Mi.

For a polydisperse sample, the ratio is always maintained $\overline{M}_z > \overline{M}_w > \overline{M}_n$. Relationship $\overline{M}_w / \overline{M}_n$ And $\overline{M}_z / \overline{M}_w$ characterize the width of the MWD.

In practice, not absolute methods for determining molecular weights are often used, but indirect methods that require preliminary calibration of the experimental value as a function of M. The most common viscometric method, which gives the average viscosity value of the molecular weight:

$$\overline{M}_\eta = \left(\frac{\int_0^\infty M^{(1+\alpha)} \rho_n(M)dM}{\int_0^\infty M \rho_n(M)dM} \right)^{1/\alpha}$$

where ρ is an experimentally determined constant in the Mark-Kuhn-Houwink equation relating the intrinsic viscosity of a polymer solution to its average viscosity molecular weight:

$[\eta] = K_\eta \overline{M}_\eta^\alpha$ (Kη is a constant depending on the type of solvent and polymer used)

The shape of the MWD curve depends on the method of polymer synthesis; it usually changes during its processing and operation. MWD curves can be uni- or polymodal and are described by various regularities.

Lecture 5

Synthesis of polymers. radical polymerization.

Plan:

1. Basic methods for the synthesis of polymers.
2. Chain and staged polymerization.
3. Initiation in radical polymerization. Photochemical polymerization. Initiators.
4. Radiation and thermal polymerization

Radical polymerizationflows through a chain mechanism.

As a result of each elementary act, a new radical is formed, to which a new neutral molecule is attached, i.e. the kinetic chain turns into a material one.

Main stagesradical polymerization:

- ***initiation***
- ***chain growth***
- ***open circuit***
- ***chain transfer***

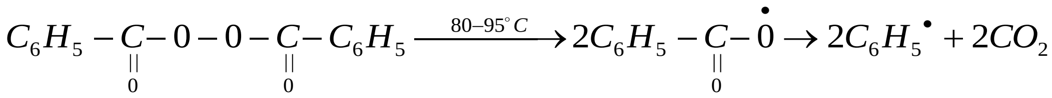
1. Initiation consists in the formation of free radicals under the action of:

- heat (thermal initiation);
- light (photoinitiation);
- ionizing radiation (radiation initiation);
- chemical initiators (chemical initiation)

The first three methods are ineffective, because accompanied by various side reactions (branching, destruction, etc.). Most often, chemical initiation is used, in which the formation of free radicals occurs due to the thermal and photochemical decomposition of various compounds containing unstable (labile) bonds, as well as as a result of OVR. The most common initiators are: peroxides, hydroperoxides, iso- and diazo compounds, perethers, acyl peroxides.

Example.

a) benzoyl peroxide

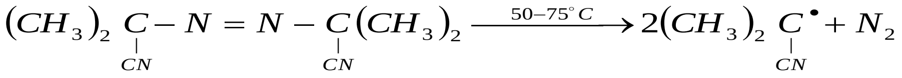


$$C_6H_5-\underset{\underset{0}{\|}}{C}-0-0-\underset{\underset{0}{\|}}{C}-C_6H_5 \xrightarrow{80-95^\circ C} 2C_6H_5-\underset{\underset{0}{\|}}{C}-\overset{\bullet}{0} \rightarrow 2C_6H_5^{\bullet}+2CO_2$$

decay t = 70 - 80˚C

Initiation efficiency f = 0.7 - 0.9

b) azobisisobutyronitrile



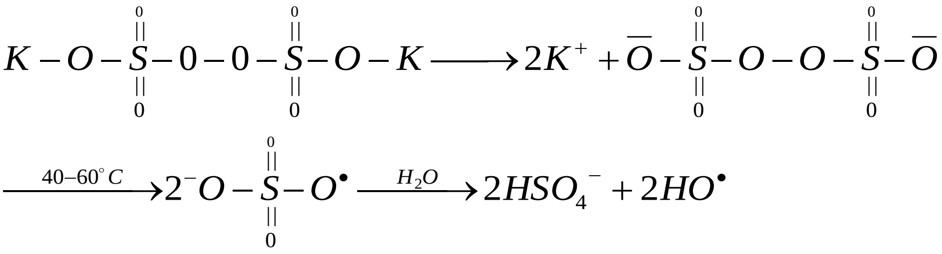
$$(CH_3)_2\underset{\underset{CN}{|}}{C}-N=N-\underset{\underset{CN}{|}}{C}(CH_3)_2 \xrightarrow{50-75^\circ C} 2(CH_3)_2\underset{\underset{CN}{|}}{C}^{\bullet}+N_2$$

decay t = 60 - 75˚C

Initiation efficiency f = 0.5 - 0.7

c) potassium persulfate

t decay = 40 - 50˚C



$$K-O-\overset{\overset{0}{\|}}{\underset{\underset{0}{\|}}{S}}-0-0-\overset{\overset{0}{\|}}{\underset{\underset{0}{\|}}{S}}-O-K \longrightarrow 2K^{+}+\overline{O}-\overset{\overset{0}{\|}}{\underset{\underset{0}{\|}}{S}}-O-O-\overset{\overset{0}{\|}}{\underset{\underset{0}{\|}}{S}}-\overline{O}$$

$$\xrightarrow{40-60^\circ C} 2\,{}^{-}O-\overset{\overset{0}{\|}}{\underset{\underset{0}{\|}}{S}}-O^{\bullet} \xrightarrow{H_2O} 2HSO_4^{-}+2HO^{\bullet}$$

The choice of initiator is determined by its solubility in the monomer or solvent and the temperature at which a certain rate of production of free radicals can be achieved.

$$E_{\text{актив}}^{\text{инициир.}} = 110 - 165 \text{кДж} / \text{моль}$$

The radical formed upon initiation adds to the double (=) bond of the monomer and starts the reaction chain.

$$R^{\bullet} + CH_2 = CHX \xrightarrow{k_и} R - CH_2 - \overset{\bullet}{C}HX$$

Since the stability of the radicals formed during the decomposition of peroxides, azo compounds, and other initiators is different, the rate of their reaction with monomer molecules, and, consequently, the rate of polymerization are different. To facilitate the decomposition of initiators and reduce the activation energy of the initiation stage, reducing agents (amines, metal salts of variable oxidation state) are introduced into the reaction.

For the purpose of downgrading $E_{\text{актив}}^{\text{инициир.}}$ (from 146 to 42 - 84 kJ / mol), redox systems are used to facilitate the decomposition of initiators.

For example:

$$H_2O_2 + Fe^{2+} \rightarrow H\underbrace{\bar{O} + HO}{}^{\bullet} + Fe^{3+}$$

$$HO^{\bullet} + H_2O_2 \rightarrow HOO^{\bullet} + H_2O$$

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + HO^{-}$$

$$Fe^{3+} + HOO^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+}$$

Redox systems are used in aqueous media or in emulsion polymerization. Their wide distribution in the polymer production industry is associated with a significant decrease in the activation energy of the decomposition of initiators into free radicals and thus a decrease in energy costs under production conditions.

2.Chain growth - consists in the sequential attachment of monomer molecules to the formed active center with its transfer to the end of the chain.

The development of a kinetic chain accompanied by the formation of a material chain.

$$RM^{\bullet} + M \xrightarrow{k_p} RMM^{\bullet}$$

$$RMM^{\bullet} + M \xrightarrow{k_p} RMMM^{\bullet}$$

$$R - [M]_{n-2} - M^{\bullet} \xrightarrow{k_p} R - [M]_{n-1} - M^{\bullet}$$

$$E_{\text{актив}}^{\text{роста цепи}} = 20 - 40 \text{кДж} / \text{моль} \text{ (small)}$$

Reaction rate constant kp = 102 – 104 (large)

The activation energy and the reaction rate constant depend on the nature of the monomers and the parameters of the reaction medium.

3. Open circuit- occurs as a result of the death of active centers.

The break of the chain leads to the break of the material and kinetic chain.

$E_{\text{актив}}^{\text{обрыва цепи}} = 8-17\,\text{кДж/моль}$

The activation energy of chain termination is determined by the diffusion activation energy radicals.

The termination can occur at any length of the growing macroradical. In this case, macromolecules of different lengths are obtained.

Breakage most often occurs in two ways: by recombination and disproportionation.

Eact ≤ 4.2 kJ/mol

$$-CH_2-\overset{\bullet}{C}HX + -CH_2-\overset{\circ}{C}HX \xrightarrow{k_0} \left| \begin{array}{l} \to -CH_2-CHX-CHX-CH_2- \\ \text{рекомбинация} \\ \to -CH_2-CH_2X + -CH=CHX \\ \text{диспропорционирование} \end{array} \right.$$

Eact \u003d 12.6-16.8 kJ / mol

Termination is also possible during the interaction of growing radicals with low molecular weight substances present in the system.

↗ by lowering the temperature ↓
You can reduce the chain breaking speed
↘ increasing viscosity ↑

4. chain transfer- occurs by detachment by a growing radical an atom or group of atoms from some molecule (chain transmitter). Wherein:

- the growing radical is converted into a valence-unsaturated molecule;
- new radical develops a kinetic chain

Thus, the chain transfer reaction consists in the fact that the substance introduced into the system - the regulator - breaks the growing chain, but at the same time it becomes a free radical itself and starts a new kinetic chain of polymerization.

An increase in temperature and an increase in the amount of chain transfer agent (eg, halogenated hydrocarbons) lead to a sharp increase in the rate of the chain transfer reaction. This reaction inhibits other polymerization steps so that individual low molecular weight substances are formed that can be separated (telomerization reaction). They contain end groups from the cleavage products of the chain transfer agent and are active in various chemical reactions, in particular for the production of new polymers.

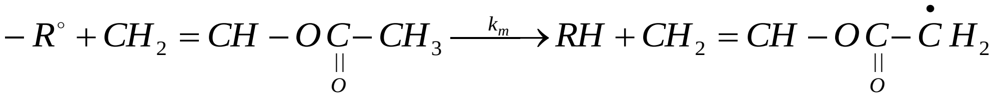
Telomeres:oligomers having reactive groups at the ends of molecules.

$$CCl_4 + M_n^{\bullet} \to ClM_n + \overset{\circ}{C}Cl_3 \quad \text{etc.}$$

$$\overset{\circ}{C}Cl_3 + M \to CCl_3M\bullet$$

Thus, ethylene telomerization in a carbon tetrachloride medium proceeds with the formation of individual products (tetrachloropentane, tetrachlorheptane, etc.)

Example. Chain transmission via:
a) a monomer molecule



$$-R^{\circ}+CH_2=CH-O\underset{\underset{O}{||}}{C}-CH_3\xrightarrow{k_m}RH+CH_2=CH-O\underset{\underset{O}{||}}{C}-\overset{\bullet}{C}H_2$$

b) solvent molecule

$$-CH_2-\overset{\circ}{C}HX+C_6H_5CH_3\xrightarrow{k_S}-CH_2-CH_2X+C_6H_5\overset{\bullet}{C}H_2$$

breakage of the material chain and further:

$$C_6H_5\overset{\bullet}{C}H_2+CH_2=CHX\rightarrow C_6H_5CH_2CH_2-\overset{\bullet}{C}HX$$

start of a new chain

c) specially introduced substances (regulators), for example, mercaptans.

$$-CH_2-\overset{\bullet}{C}HX+RSH\xrightarrow{k_S}-CH_2-CH_2X+RS\bullet$$

$$RS\bullet+CH_2-CHX\rightarrow RSCH_2-\overset{\bullet}{C}HX$$

km , ks are the chain transfer rate constants.

When interacting growing radical with the chain transmitter molecule stops the growth of the material chain, i.e. the molecular weight of the resulting polymer is reduced; the kinetic chain is preserved.

The ability to participate in chain transfer during radical polymerization is characterized by the constant of chain transfer to the monomer Cm, to the solvent Cs, to the initiator Cu.

$$C_s=\frac{k_s}{k_p}\qquad C_m=\frac{k_m}{k_p}\qquad C_u=\frac{k_u}{k_p}$$

Cm = (0.1 - 5) * 10-4 - small value

For example, during polymerization vinyl acetate Cm = 2·10-3
Of the solvents, a high Cs value in CCl_4. Thus, during the polymerization of styrene Cs = 9·10-3

Mechanism of radical polymerization.

Polymerization in which the active growth sites are free radicals. Radical polymerization is possible for most vinyl, vinylidene, diene monomers, as well as for some intense cyclic. connections. Some unsaturated monomers are not capable of radical polymerization due to steric hindrance (eg 1,2-disubstituted vinyl monomers) or in case of degenerate chain transfer, eg. propylene, allyl monomers.

Radical polymerization is one of the main industrial methods by which more than half of the polymers produced in the world are obtained, including polyethylene (high pressure), polystyrene, copolymers of ethylene and styrene with various polar monomers, polyvinyl chloride, polyacrylates and polymethacrylates, a number of synthetic rubbers and water-soluble carbon chain polyelectrolytes. The kinetic scheme of radical polymerization includes four elementary stages: initiation, growth, transfer, and chain termination. At the initiation stage, primary monomer radicals are formed as a result of direct energy exposure (heat, UV or ionizing radiation; the last two are radiation polymerization) or, more often, with interaction. monomer with radicals arising from homolytic. decomposition of specially introduced radical initiator substances (for example, peroxides,

To increase the rate of initiation at low temperatures, reducing agents are added to peroxides, for example. transition metal salts or amines (so-called redox initiators). Stage initiation includes at least two consecutive. elementary act - generation of R• radicals (reaction 1, a) and their interaction with the monomer (reaction 1, b): (I-initiator, M-monomer, M•1-primary monomer radical, k1 and k'1 - rate constants corresponding reactions).

In addition to reactions (1, b), R• radicals can participate in side reactions, which is taken into account using the coefficient. initiation efficiency (f); the latter characterizes the ratio of the number of radicals involved in p-tion (1, b) to the total number of radicals formed in p-tion (1, a). The values of f are usually 0.6-0.8, and k1 and have the order of 10-5-10-4 s-1 and 10-103 l/(mol s) respectively, therefore in mol/l) in the reaction medium; thus, act (1, a) kinetically determines the stage of initiation: where u1 is the rate of initiation.

The main stage of polymerization, the chain growth reaction, upon repeated repetition of which a macromolecular chain is formed, is described by the equation: (M • n-macroradical containing n monomeric units). The growth reaction rate is expressed by the equation: It is assumed that the reaction. the ability of macroradicals does not depend on their length; as a rule, such an assumption is valid for n > 3-5. The kinetic parameters of reaction (3) are given in Table. 1. The values of k2 depend on two factors - the reactivity (activities) of the monomer and the macroradical, which, as a rule, change in opposite directions, since the reaction. the ability of the monomer in the presence of conjugated bonds in its molecule increases, and the macroradical decreases. Of these two factors, the macroradical activity has a decisive influence on the chain growth rate, therefore, the sequence of arrangement of monomers in table. 1 reflects the growth of reactions. ability of macroradicals. reaction the ability of monomers and radicals also depend on the polar and steric. factors, naib. fully manifested in p-tions of copolymerization or other competing p-tions. The speed and direction of radical p-tions usually depend little on the characteristics of the reactions. environment.

However, if there is a specific interactions of the monomer and (or) radical with the molecules of the environment, for example. in the formation of p-complexes, donor-acceptor complexes, complexes involving Lewis to-t or hydrogen bonds, a change in the chain growth rate constants is observed. The addition of monomers during radical polymerization occurs predominantly. head-to-tail: The proportion of links connected head-to-head and tail-to-tail usually does not exceed several. percent and decreases during the polymerization of monomers containing bulk substituents X. At the same time, stereoregular addition does not occur. So, during the radical polymerization of vinyl monomers, atactic compounds are formed. polymers with a certain predominance of syndiotactic. structures. Reducing the t-ry polymerization contributes to an increase in the proportion of syndiotactic. structures. Limitation of growing chains during radical polymerization is possible by chain termination and (or) transfer. Chain termination is an irreversible chem. deactivation of growing chains usually proceeds as a result of disproportionation of two macroradicals (p-tion 6, a) or their recombination (6, b): . (and -rate constants of the corresponding districts). The contribution of districts (6, a) or (6, b) to the overall termination rate is determined by the activity of the interacting macroradicals and steric. factors: for inactive radicals and in the presence of small substituents X in the monomer, as a rule, termination by the recombination mechanism is characteristic. The chain termination reaction rate is expressed by the equation: Chain termination is an irreversible chem. deactivation of growing chains usually proceeds as a result of disproportionation of two macroradicals (p-tion 6, a) or their recombination (6, b): . (and -rate constants of the corresponding districts). The contribution of districts (6, a) or (6, b) to the overall termination rate is determined by the activity of the interacting macroradicals and steric. factors: for inactive radicals and in the presence of small substituents X in the monomer, as a rule, termination by the recombination mechanism is characteristic. The chain termination reaction rate is expressed by the equation: Chain termination is an irreversible chem. deactivation of growing chains usually proceeds as a result of disproportionation of two macroradicals (p-tion 6, a) or their recombination (6, b): . (and -rate constants of the corresponding districts). The contribution of districts (6, a) or (6, b) to the overall termination rate is determined by the activity of the interacting macroradicals and steric. factors: for inactive radicals and in the presence of small substituents X in the monomer, as a rule, termination by the recombination mechanism is characteristic. The chain termination reaction rate is expressed by the equation: (and -rate constants of the corresponding districts). The contribution of districts (6, a) or (6, b) to the overall termination rate is determined by the activity of the interacting macroradicals and steric. factors: for inactive radicals and in the presence of small substituents X in the monomer, as a rule, termination by the recombination mechanism is characteristic. The chain termination reaction rate is expressed by the equation: (and -rate constants of the corresponding districts). The contribution of districts (6, a) or (6, b) to the overall termination rate is determined by the activity of the interacting macroradicals and steric. factors: for inactive radicals and in the presence of small substituents X in the monomer, as a rule, termination by the recombination mechanism is characteristic. The chain termination reaction rate is expressed by the equation:

Bimolecular chain termination is a diffusion-controlled p-tion, consisting of three consecutive. stages: 1) post-path, diffusion of two macroradicals with the formation of a united coil; 2) mutual approach of the active ends due to the diffusion of individual links and chain segments; 3) directly. chem. reaction interaction. centers with the formation of inactive macromolecules. For most of the studied vinyl monomers, k3 is inversely proportional to the viscosity of the initial system, and the termination rate is limited by stage 2. Thus, factors that reduce the mobility of chain segments (the introduction of a comonomer that increases the chain rigidity, a decrease in the polymerization temperature, etc.) significantly reduce the rate of bimolecular termination . Chain transfer - a reaction leading to the transfer of the active center from the growing macroradical to any other molecule (solvent, monomer, initiator, polymer), acting as a transfer agent (A), with the formation of a "dead" macromolecule (Mn) and a new active center (A•): (k4 is the chain transfer rate constant). Usually p-tion chain transfer leads to the continuation of the kinetic. chains, since the new radical A • is able to initiate radical polymerization at a rate close to the rate of p-tion growth. Otherwise, degenerate chain transfer takes place (i.e., chain growth occurs at a lower rate on A• than on the macroradical) or inhibition of radical polymerization (see Inhibitors). Main chain transfer p-transfer of a mobile H or Hal atom from the transfer agent to the macroradical, less often in the opposite direction. The rate of chain transfer p-tion and the place where the H or Hal atom is cleaved are determined by the energy of the C-H, S-H, C-Hal bond breaking in the molecule of the transfer agent, etc. So, the rate of elimination of H atoms in sat. hydrocarbons decreases in the series: hydrogen at the tertiary atom C> at the secondary > primary. R-tion transfer chains compete With R-tion growth, so for quantities. transfer characteristics usually use transfer constants C=k4/k2, according to which they judge the reaction. abilities of transfer agents.

Intramolecular and intermolecular chain transfer reactions on the polymer lead to the formation of macromolecules with short chain branches, crosslinked or grafted copolymers. In practice, district transfer chains are used to regulate the pier. the mass of the polymer and for the synthesis of graft copolymers (by transferring the chain to the polymer). In the first case, transfer agents with C>10-3 are used, to-rye called. regulators say. masses. At C1, low mol. products. At the initial stages of the transformation, radical polymerization, as a rule, proceeds at a constant rate, which is associated with the fulfillment of the condition of quasi-stationarity (constancy of the concentration of active centers): Since the monomer is consumed by Ch. arr. at the stage of chain growth, the total rate v of radical polymerization is practically equal to the rate of this stage and can be. is determined by substituting expression (9, a) into equation (4): First order in monomer and half in initiator max. typical of radical polymerization. Dr. the most important kinetic parameter of radical polymerization is the average mol. the mass, or the average degree of polymerization, of the resulting polymer is determined by the ratio of the chain growth rate to the sum of the chain termination and transfer rates: Under conditions of quasi-stationarity and chain termination by disproportionation, the following equation is valid: (S). In the case of chain termination by recombination of radicals, the factor 1/2 is introduced into the first term. The CM value determines the top. possible limit. For vinyl monomers, therefore, high mol. polymers. At the same time, due to the high values of Cm of monomers of the allyl series (for example, for allyl acetate Cm0.1),

The polymers formed during radical polymerization are characterized by a wide molecular weight distribution (MWD), the detailed nature of which is under homologous conditions. process is determined by the mechanism of limiting growing chains. So, when growing chains are limited by p-tions of disproportionation and (or) transfer = 2 (where and are respectively the average mass and number average molecular weights), and when broken by recombination = 1.5. With the parallel implementation of both p-tions of the bimolecular breakage, this ratio has an interval. meaning. With radical polymerization to deep degrees of conversion of monomers or with the formation of an insoluble polymer, a significant increase is observed. broadening of the MWD up to the appearance of a polymodal MWD.

Lecture 5

Kinetics of radical polymerization

Plan:

1. Kinetics of radical polymerization.
2. Factors affecting the kinetics of radical polymerization.
3. General formula for the kinetics of radical polymerization
4. Thermodynamics of polymerization.

1. Kinetics of radical polymerization.

The process speed is described by the equation: $-\frac{dM}{d\tau} = \upsilon_u + \upsilon_p$, Where

$-\frac{dM}{d\tau}$ - monomer disappearance rate

υ_u And υ_p - rate of chain initiation and growth

When a high molecular weight polymer is formed, the number of monomer molecules participating in the initiation stage is much less than in the growth stage, therefore υ_u can be neglected.

$$-\frac{dM}{d\tau} = \upsilon = \upsilon_p = k_p[R^\circ][M]$$

$[R^\circ]$ hard to measure. For a stationary process, the rate of appearance of a radical is equal to the rate of their death, and the rate of change in the concentration of radicals ($\upsilon_u = \upsilon_0$)

$$\frac{d[R^\circ]}{d\tau} = 0$$

For a stationary process, the polymerization rate equation will take the form:

$$\upsilon = k_p\left(\frac{k_u}{k_0}\right)^{0,5} \cdot [J]^{0,5}[M]$$

$[J]$-concentration of initiator (known and set before the start of the reaction)

It follows from the equation that the rate of polymerization depends on the rate of initiation to the power of 0.5, i.e. increase υ_u doubling leads to an increase $\upsilon_{полимер.}$ V $\sqrt{2}$ once. This is explained by the bimolecular mechanism of chain scission.

During thermal initiation, the polymerization rate V depends on the ratio of the three reaction rate constants $k_p\left(\frac{k_u}{k_0}\right)^{0,5}$

A typical kinetic curve describing monomer conversion (i.e., the conversion of a monomer to a polymer as a result of polymerization) as a function of time is S-shaped.

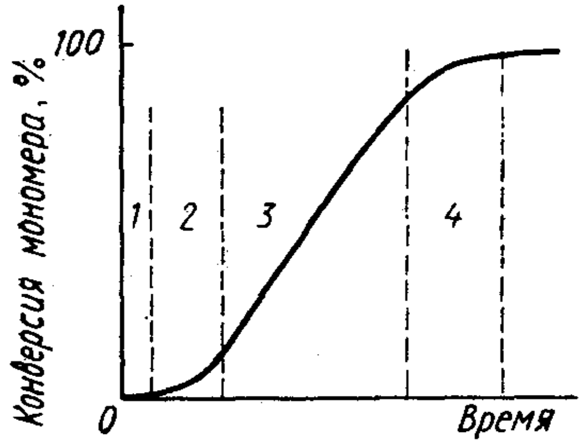


Fig.1 Typical kinetic curve of chain radical polymerization:
1 - inhibition; 2 - acceleration of polymerization (the rate increases with time); 3 – stationary period (polymerization rate is constant); 4 - polymerization slowdown (speed decreases with time)

As can be seen from fig. 1 on the curve, five sections can be distinguished according to the rates of the main reaction of the transformation of the monomer into a polymer as a result of polymerization:

1 – site of inhibition, where the concentration of free radicals is low. And they cannot start the chain polymerization process;

2 - polymerization acceleration section, where the main reaction of monomer-to-polymer transformation begins, and the rate increases;

3 – section of the stationary state, where the polymerization of the main amount of the monomer occurs at a constant rate (rectilinear dependence of the conversion on time);

4 - reaction deceleration region, where the reaction rate decreases due to a decrease in the content of free monomer;

5 - termination of the main reaction after the exhaustion of the entire amount of the monomer.

Of greatest interest is the stationary period of the polymerization reaction, when polymerization of the bulk of the monomer occurs at a constant rate. This is possible when the number of newly formed free radicals (stage of initiation) is equal to the number of disappearing macroradicals (stage of termination) of the reaction and material chains.

Degree of polymerizationn (i.e., the number of units of monomeric units in one statistically average macromolecule) is, by definition, proportional to the chain propagation reaction rate and inversely proportional to the chain termination reaction rate, since a neutral macromolecule is formed as a result of the collision of two growing macroradicals.

$n=\upsilon p/\upsilon rev=kp[M^*][M]/krev[M^*]2= kp[M]/krev[M^*] = kn/[M^*] =knI /[I]0.5$

In other words, the degree of polymerization, and hence the average molecular weight of the polymer in free radical polymerization, is inversely proportional to the square root of the initiator concentration.

Lecture 7

Thermodynamics of polymerization.

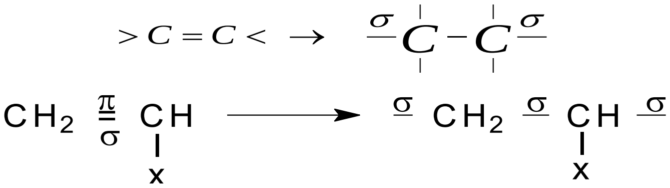
Plan:

1. Changes in enthalpy and entropy in radical polymerization.
2. Influence of the chemical structure of the monomer on polymerization.
3. High conversion polymerization.

Thermodynamics of polymerization.

The polymerization ability of unsaturated compounds depends on the location of the bonds, the nature and number of substituents. The general patterns of polymerization of such compounds were first demonstrated by S. V. Lebedev.

During the polymerization of unsaturated hydrocarbons, one double bond is broken, forming two single bonds, and heat is released.



$$>C=C<\ \rightarrow\ \overset{\sigma}{-}\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\overset{\sigma}{-}$$

$$CH_2 \overset{\pi}{\underset{\sigma}{=}} \underset{X}{\underset{|}{CH}} \longrightarrow \overset{\sigma}{-}CH_2\overset{\sigma}{-}\underset{X}{\underset{|}{CH}}\overset{\sigma}{-}$$

π - bond breaking creates two σ-bonds.

Since the bond energy C = C (π) is 145.5 kcal / mol, and the bond energy C - C - (σ) is 84 • 2 kcal / mol, the difference determines the magnitude of the heat effect of the reaction: 84 x 2 - 145.2 \u003d 22.5 kcal/mol

Polymerization at high convention.

The transformation of monomers π-bonds into polymeric σ-bonds is characterized by heat release. Ideally, this heat is 22.4 kcal mol (94 kJ mol). This means that the polymerization of vinyl monomers is an exothermic process. The heat of polymerization of most monomers is less than this value, which requires additional energy, which means that polymerization may not occur as a result of the appearance of steric effects.

With an increase in the degree of conversion of the monomer in the course of radical polymerization, creatures occur. changes in composition and physical reaction properties environment, to-rye are reflected in the kinetics of the district and the characteristics of the resulting products. Yes, that means. an increase in the viscosity of the reaction. environment primarily limits the diffusion mobility of macroradicals and, therefore, reduces the rate of termination, leading to an increase in the rate of radical polymerization and mol. the mass of the resulting polymer (gel effect). In the case of the formation of an insoluble polymer, such phenomena manifest themselves already at the beginning of the process due to the immobilization (“sticking”) of growing chains in the polymer matrix.

Polyfunction is widely used in radical polymerization. initiators, monomers, chain transfer agents, re-participation to-rykh during polymerization changes the structure of the polymer or kinetic. characteristics. So, polyinitiators are able to give radical polymerization kinetic. patterns of polycondensation, from polyfunction. monomers are formed cross-linked polymers, and the introduction of polyfunction. chain transfer agents results in star-shaped polymers. Radical polymerization can be carried out in bulk, emulsion, suspension, solution, and other media

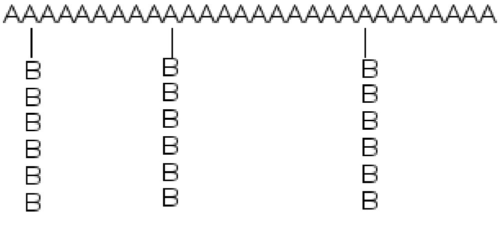
Lecture 8

Copolymerization.

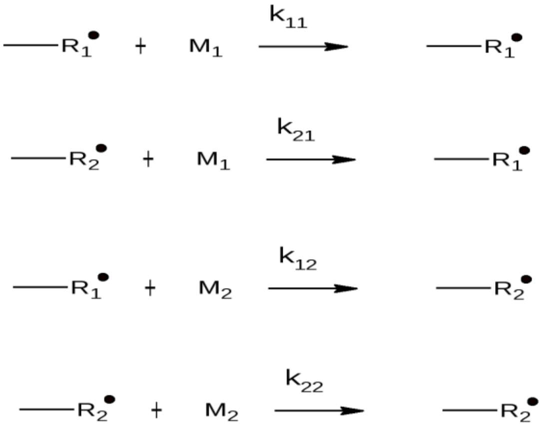
Plan:

1. The concept of copolymerization.
2. Copolymerization reactions. Mayo-Lewis equation.
3. Constants withpolymerization and methods for their determinationnia. Q—e scheme of Alfrey-Price.

Various approaches can be used to obtain molecules with complex architecture: different types of polymerization, different initiators, solvents and reaction conditions can be used; it is also possible to copolymerize different monomers or modify already obtained polymers. Some examples of copolymers are shown in the table.

Copolymer type	**Schematic structure**	**Designation**
Block	AAAAAAAAAAAABBBBBBBBBBBB	poly(A)-block-poly(B)
Alternate	ABABABABABABABAB	poly(A-alt-B),poly(AB)
Statistical	AABABAABBBAABBBABAABABAAB	poly(A-stat-B)
Graft		poly(A)-graft-poly(B)
Variables	AAAAABAAABAABBABBBBBBBBB	poly(A-grad-B)

When developing a copolymerization technique, it is necessary to take into account the relative reactivity of the monomers. The kinetics of copolymerization can be described by a set of elementary reactions with corresponding rate constants. In the case of radical copolymerization of two monomers, four elementary chain propagation reactions are possible (terminal link model):



The relative reactivity of monomers during copolymerization is characterized by the ratio of the constants of addition to the macroradical of “own” and “foreign” monomers:

$$r_1 = \frac{k_{11}}{k_{12}}\text{, And}\qquad r_2 = \frac{k_{22}}{k_{21}}.$$

These ratios are called copolymerization constants and take values from zero to 1. For example, for styrene and maleic anhydride, the copolymerization constants are 0.04 and 0.01, respectively. Sometimes this approach is used to determine the constants of binary ionic copolymerization.

Copolymerization kinetics

In the reaction of monomers $M_1$and M2 with free radicals formed during the splitting of the initiator, new radicals are formed, one of which ends with the last bond, and the other with the last:

$$R^\bullet + M_1 \to M_1^\bullet$$
$$R^\bullet + M_2 \to M_2^\bullet$$

Each of the resulting radicals can react both with the monomers M_1, and with M2.

$$1)\ M_1^\bullet + M_1 \xrightarrow{K_{11}} M_1 - M_1^\bullet \quad V_r = K_{11}[M_1^\bullet][M_1]$$
$$2)\ M_1^\bullet + M_2 \xrightarrow{K_{12}} M_1 - M_2^\bullet \quad V_r = K_{12}[M_1^\bullet][M_2]$$
$$3)\ M_2^\bullet + M_2 \xrightarrow{K_{22}} M_2 - M_2^\bullet \quad V_r = K_{22}[M_2^\bullet][M_2]$$
$$4)\ M_2^\bullet + M_1 \xrightarrow{K_{21}} M_2 - M_1^\bullet \quad V_r = K_{21}[M_2^\bullet][M_1]$$

Here, reactions (1) and (3) are called homopolymerization, and reactions (2) and (4) are called transverse growth. The monomer participates only in reactions (1) and (4), so its consumption rate is represented by the following equation:

$$-\frac{d[M_1]}{dt}=k_{11}[M_1^\bullet][M_1]+k_{21}[M_2^\bullet][M_1] \qquad (5)$$

The consumption rate of the monomer M2 is calculated similarly:

$$-\frac{d[M_2]}{dt}=k_{22}[M_2^\bullet][M_2]+k_{12}[M_1^\bullet][M_2] \qquad (6)$$

Dividing (5) by equation (6) gives the following expression:

$$\frac{dM_1}{dM_2}=\frac{k_{11}[M_1^\bullet][M_1]+k_{21}[M_2^\bullet][M_1]}{k_{22}[M_2^\bullet][M_2]+k_{12}[M_1^\bullet][M_2]} \qquad (7)$$

Due to the fact that elementary reactions (2) and (4) occur many times in the process of chain growth, that is, they quickly turn into $M_1^\bullet$ on $M_2^\bullet$, V $M_2^\bullet$ on $M_1^\bullet$ the following equation is formed:

$$k_{12}[M_1^\bullet][M_2]=k_{21}[M_2^\bullet][M_1] \qquad (8) \text{ from here}$$

$$[M_2^\bullet]=\frac{k_{12}[M_1^\bullet][M_2]}{k_{21}[M_1]} \qquad (9)$$

Indeed, if you look $M_2^\bullet + M_1 \rightarrow M_1^\bullet$ to the reaction

$$M_1^\bullet + M_2 \rightarrow M_2^\bullet$$

the faster the reaction, the higher $M_2^\bullet$ concentration in the reaction mixture, which leads to acceleration $M_2^\bullet$ reaction (2), the rate of which is proportional to the concentration of the above reactions. Similarly, if the transition speed $M_1^\bullet$ on $M_2^\bullet$ in higher than u, $M_2^\bullet$ on $M_1^\bullet$ then the transition speed is higher. In equation (8), we replace $k_{21}[M_2^\bullet][M_1]$ on [[$M_2^\bullet$]] and replace its value $[M_1]/k_{12}$; Now multiplying and $[M_1^\bullet]$ reducing the image and the denominator on the right side of the resulting equation, we get the following Mayo and Lewis copolymerization differential equation:

$$\frac{d[M_1]}{d[M_2]}=\frac{[M_1]}{[M_2]}\cdot\frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]} \qquad (10)$$

Here, $\frac{k_{11}}{k_{21}}=r_1$ And $\frac{k_{22}}{k_{21}}=r_2$ equals.

Copolymerization diagram

$$\frac{[m_1]}{[m_2]}=\frac{[M_1]}{[M_2]}-\frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_2]}$$

Copolymerization is called constants $r_1$and r2-copolymerization in the composition equation. Their values depend on the chemical nature of the monomers involved in the reaction. The dependence of the composition of the copolymer on the composition of the mixture of monomers is characterized by a composition diagram. The shape of this diagram depends on the values of r1 and r2. Figure 1 shows different chart shapes corresponding to different values of r1 and r2:

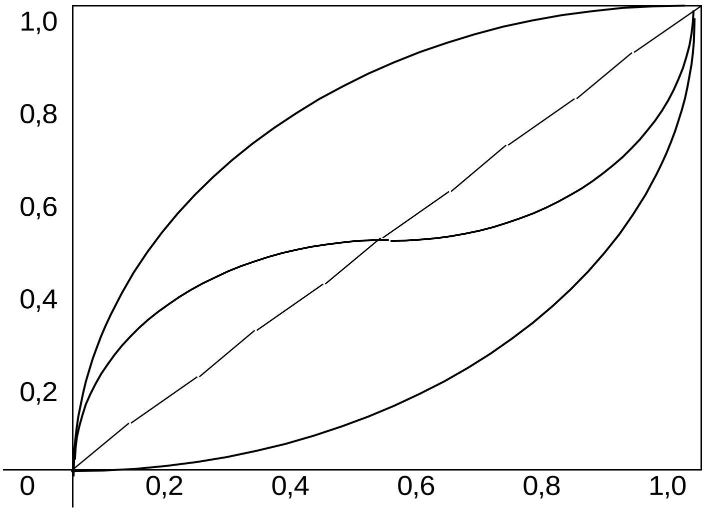


Fig.1. Scheme of the composition of the copolymerization reaction
Molar part M_2-monomer is initially in the mixture.
Mole fractionm2-monomer in the composition of the copolymer.

Lecture 9

Calculations using copolymerization constants.

Plan:

1. Copolymerization constants and methods for their determination.
2. Q—e scheme of Alfrey-Price.
3. Compositional heterogeneity of copolymers in composition. Microstructure of the copolymer chain.

Copolymerization constants and methods for their determination

There are several methods for determining copolymerization constants, which are divided into graphical and analytical.

MAYYO-LUIS METHOD

(How to cross lines on a graph)

In this method, by changing the composition equation

$$\frac{[m_1]}{[m_2]} = \frac{[M_1]}{[M_2]} - \frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_2]} = \frac{r_1\frac{M_1}{M_2}+1}{1+r_2\frac{M_2}{M_1}}$$

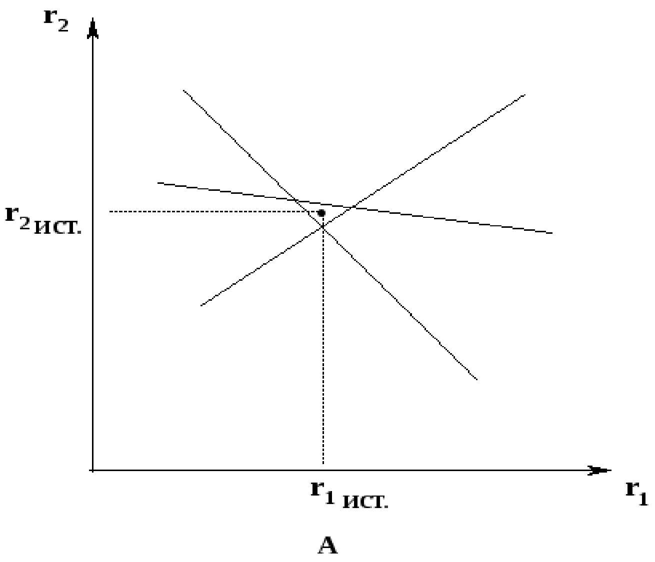
copolymers, the following equation is formed, which shows that the value of r2 is linearly related to r1:

$$r_2 = \frac{[M_1]}{[M_2]}\left\{\frac{[m_2]}{[m_1]}(1+\frac{[M_1]}{[M_2]}\cdot r_1)-1\right\} \qquad (1)$$

$[M_1]$, [M2] - initial concentrations of monomers M1 and M2:

[m1], [m2] - concentrations of monomers [M1], [M2] in the copolymer.

Each pair of values $[M_1]$, [M2] and [m1], [m2] gives a straight line in the coordinate system r1 and r2.



1. Mayo-Lewis method

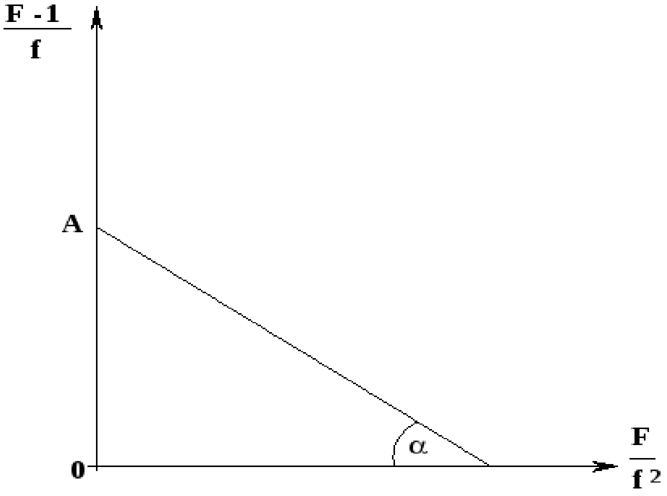
The point of intersection of the calculated lines for several experiments corresponds to the desired values of r1 and r2. Due to some errors in experiments, these lines usually do not intersect at the same point, but intersect, forming a triangle. The coordinates of the center of the triangle give the values r1 and r2. To find the values of r1 and r2, special experiments are carried out. The amount of copolymer formed should not exceed 10%.

Fineman-Ross method

Denoting d[A]/d[B] as F and [A]/[B] as f, and after a series of transformations, the Mayo-Lewis equation is brought to the form:

$$\frac{F-1}{f} = r_1 - \frac{F}{f^2} \cdot r_2$$

Using the values of [A] and [B] and the found values of d[A] and d[B], calculate the values of F and f for each mixture of monomers, and then build a graph in the coordinates F/f2 - (F-1)/f ; it is a straight line (Fig. 4b). This straight line cuts off the value r1 on the y-axis (segment 0A); tangent of the slope of the straight line to the abscissa axis (tgα) gives the value of r2.



Б

2. Fineman-Ross method

Theoretical calculation of copolymerization constants
(Q—e scheme of Alfrey-Price)

As already mentioned, the copolymerization constants characterize the comparative reactivity of the monomers and the radicals formed in the reaction, i.e. they are directly related to their structure. This makes it possible in principle to calculate the copolymerization constants a priori.

So far, it has not been possible to find exact quantitative regularities relating the values of the copolymerization constants to the structure of the particles involved in the process. However, it was possible to find some correlation dependences, which, to some extent empirically, make it possible to predict the values of the copolymerization constants (of course, only with a certain degree of approximation). Among these correlation dependences, the most well-known is the so-called Q-e scheme of Alfrey-Price (Alfrey-Price, 1947).

According to this scheme, the affinity of the polymer radical and the monomer (which determines the easiness of any elementary chain propagation reaction) is determined by the following factors:); 2) factor Q - a value characterizing the activity of the monomer (for monomer A - Q1, for monomer B - Q2); 3) the factor e is a value that characterizes the polarity of the monomer and the corresponding radical (for A and ~A▪ - e1, for B and ~B▪ - e2). For simplicity, it is assumed that the polarity factor for the monomer and the corresponding radical is the same. This, in fact, is not quite correct, but it does not noticeably worsen the correlation. At the same time, for electron-rich monomers (for example, vinyl monomers containing a donor substituent X at C=C - bonds,

According to Alfrey-Price, the rate constants of elementary chain propagation reactions in radical copolymerization are related to these factors as follows:

$$\mathbf{k_{11} = P_1Q_1\exp(-e_1^2) \qquad k_{22} = P_2Q_2\exp(-e_2^2)}$$

$$\mathbf{k_{12} = P_1Q_2\exp(-e_1e_2) \qquad k_{21} = P_2Q_1\exp(-e_2e_1)}$$

Следовательно, для констант сополимеризации:

$$\mathbf{r_1 = \frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2}\exp[-e_1(e_1 - e_2)]}$$

$$\mathbf{r_2 = \frac{k_{22}}{k_{21}} = \frac{Q_2}{Q_1}\exp[-e_2(e_2 - e_1)]}$$

Thus, to calculate the copolymerization constants, it is necessary to know the values of the factors Q and e. In this case, it is not the absolute values of these factors that are important here, but their ratio for different monomers (the above equations are correlation equations). Therefore, here, as a “starting point”, one can choose a certain “reference” monomer, assign to it some, in general, arbitrary values of the factors Q and e (however, on condition that the order and sign of these factors are somehow consistent with the structure of the monomer) , and then experimentally compare other monomers with the reference one.

Styrene was chosen as the reference monomer (perhaps the most "universal" monomer); the values were assigned to it: Q = 1, e = - 0.8. To determine the values of the Q and e factors for any monomer, it is copolymerized with styrene and the copolymerization constants r1 and r2 are experimentally determined. The found values of the constants are substituted into the above equations and two equations are obtained with two unknowns Q2 and e2 (because Q1 = 1, e1 = - 0.8); the solution of the equation gives the desired values.

In this way, the values of the Q and e factors were experimentally determined for many monomers; by choosing any pair of these monomers, one can calculate the copolymerization constants for this pair (for the same conditions in which the values of Q and e were determined. The reliability of these calculations is far from 100%, but still allows one to predict the order of magnitude of the copolymerization constants and their ratio, and in many cases, assign a pair of monomers to one of the four groups mentioned above.

An analysis of the Alfrey-Price equations above shows that if the polarity of the monomers is opposite (the factors e have different signs), then both copolymerization constants will be less than unity, i.e. the copolymer will tend to alternate. Therefore, if, for example, the task is to obtain a partially alternating copolymer of two vinyl monomers, you need to choose a pair where one monomer contains a donor substituent in the C=C bond, and the other is an acceptor substituent. There is an assumption that such a "donor-acceptor" pair of monomers forms a charge-transfer complex, which increases the rate of copolymerization and further promotes alternation.

The study of copolymerization, in addition to its obvious applied interest, is also of very important theoretical significance, since it makes it possible to obtain important information about the reactivity of monomers.

The patterns of copolymerization of three monomers are in principle similar to those described above, but the calculations here are more cumbersome (for example, it is necessary to take into account not two, but six copolymerization constants).

The regularities of radical copolymerization considered here are in many respects applicable to ionic copolymerization as well. The formation of a copolymer chain, as in radical processes, proceeds at the stage of growth according to the chain mechanism, through the interaction of the active center with the monomer.

Lecture 10

Ionic polymerization.

Plan:

1. Reactions of cationic polymerization.
2. Catalysts and co-catalysts.
3. Mechanism of cationic polymerization.
4. Kinetics of cationic polymerization.

Ionic polymerization is a process of polymer synthesis in which ions are active centers that initiate a chain reaction. Ionic polymerization proceeds in the presence of catalysts. Ionic polymerization catalysts can be divided into three classes:

1) compounds - donors of protons: Bronstende acids (HF, HCl, etc.) and especially Lewis acids (AlCl3 + HCl, BF3 + HF, etc.);

2) compounds are electron donors;

3) Ziegler-Natta catalysts.

Catalysts of the first group are ineffective for many compounds with electron-withdrawing substituents at the double bond (styrene, α-vinylpyrrolidone), but they are very active with respect to substances such as vinyl compounds with conjugated bonds -

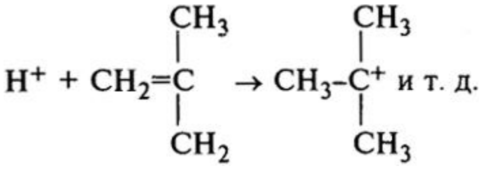
C=O and -C≡N.

Catalysts of the second group promote the polymerization of vinyl compounds with increased electron density at the double bond.

Ziegler-Natta catalysts form a coordination complex with the monomer molecule. Therefore, the synthesis of polymers in the presence of these catalysts is called ion-coordination polymerization.

Depending on the charge of the resulting ion, cationic and anionic polymerization are distinguished.

Cationic or carbonium polymerization proceeds with the formation of a carbonium ion, a polar compound with a trivalent carbon atom bearing a positive charge. Catalysts are substances active in Friedel-Crafts reactions. The catalyst is an acceptor, and the polymerizable monomer is an electron donor:



$$H^+ + CH_2{=}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2}{C}} \rightarrow CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^+}} \text{ и т. д.}$$

Ionic polymerization is accelerated in the presence of cocatalysts.

In cationic polymerization, hydroxyl-containing compounds (water, alcohols, acids) serve as cocatalysts; polymerization cocatalysts in the presence of alkyl metals (Ziegler-Natta catalysts) are chlorides of metals of variable valence, for example TiCl3. The rate of ionic polymerization is very high. The mechanism of ionic polymerization includes several stages.

The origin (excitation) of the chain consists of the following stages:

for the carbonium process -

1) the formation of a complex anion and a proton (Lewis acid)

BF3 + C2H5OH ⇄ [BF3OC2H5]-H+,

2) monomer activation

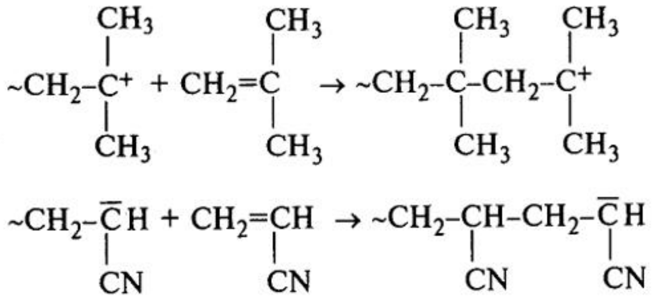
H+ + CH2=C(CH3)2 → CH3 - C+(CH3)2;

for the carbanion process -

The continuation (growth) of the chain is carried out by attaching the monomer to the monomer ion. The regular structure of macromolecules upon the sequential addition of head-to-tail monomers is determined by the polarity and size of the side substituent and the orienting effect of the catalyst particles.

The flow of the ionic polymerization process can be illustrated by the following scheme:

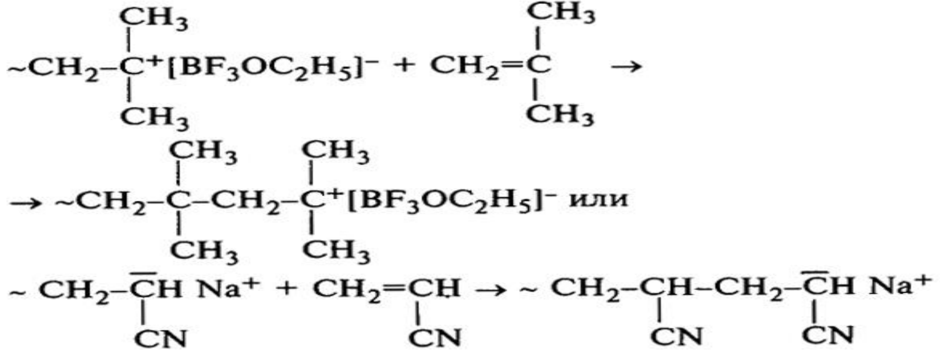
1) polymerization with the participation of a free ion proceeds according to the scheme



$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^+}} + CH_2=\overset{CH_3}{\underset{CH_3}{C}} \rightarrow \sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C^+}}$$

$$\sim CH_2-\underset{CN}{\bar{C}H} + CH_2=\underset{CN}{CH} \rightarrow \sim CH_2-\underset{CN}{CH}-CH_2-\underset{CN}{\bar{C}H}$$

2) ion-pair polymerization includes the following stages of a chain process:



$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^+}}[BF_3OC_2H_5]^- + CH_2=\overset{CH_3}{\underset{CH_3}{C}} \rightarrow$$

$$\rightarrow \sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C^+}}[BF_3OC_2H_5]^- \text{ или}$$

$$\sim CH_2-\underset{CN}{\bar{C}H}\ Na^+ + CH_2=\underset{CN}{CH} \rightarrow \sim CH_2-\underset{CN}{CH}-CH_2-\underset{CN}{\bar{C}H}\ Na^+$$

The chain transfer to the solvent can proceed according to the scheme

$$\sim CH_2-\overset{+}{C}(CH_3)_2[BF_3OC_2H_5]^- + CH_3NO_2 \rightarrow$$

$$\rightarrow -CH_2-CH(CH_3)_2 + [BF_3OC_2H_5]^-[CH_2NO_2]^+.$$

In contrast to radical polymerization, the rate constants of growth, chain termination, and chain transfer during ionic polymerization are characteristic not for one or another monomer, but only for a certain monomer-catalyst-cocatalyst-solvent system, because the counterion is located close enough, having a significant effect on the reactions of the ionized end growing chain, and the degree of ionization depends on the nature of the solvent.

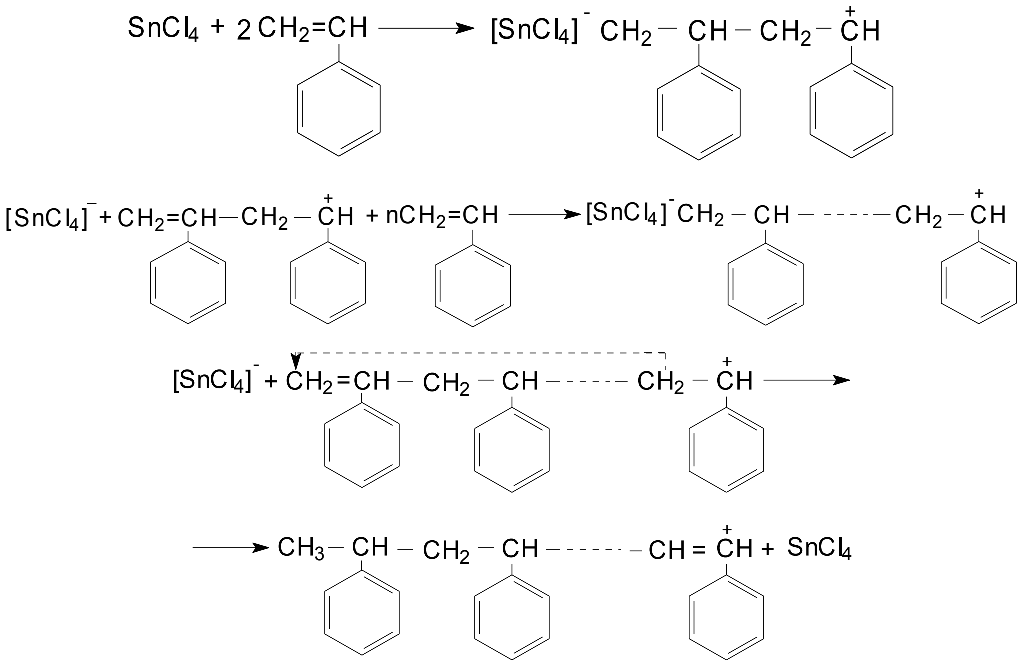
The addition of a cocatalyst in amounts not exceeding the stoichiometric ratio with the catalyst increases the rate of the process, but reduces the degree of polymerization of the resulting polymer. The average degree of polymerization is directly proportional to the monomer concentration and does not depend on the catalyst concentration:

$$\overline{P}_n = K_n[\mathrm{M}].$$

The active "end" of the growing macromolecule is in the field of action of the counterion. As a result, each new monomer molecule, approaching the growing chain, finds itself in a polarizing field formed by two opposite charges, and, orienting itself in the necessary way, is included in the macromolecule (macrocation) in a certain order.

The polymers obtained as a result of ionic polymerization are characterized by a more regular primary structure than in free radical processes.

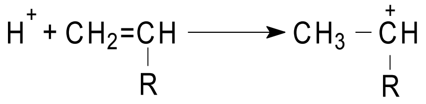
Mechanism of cationic polymerization



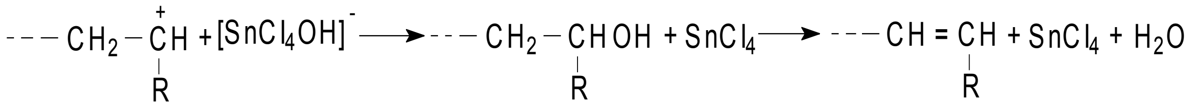
In the presence of a cocatalyst:

$$SnCI_4 + H_2O \rightarrow [SnCI_4OH]^- + H^+$$

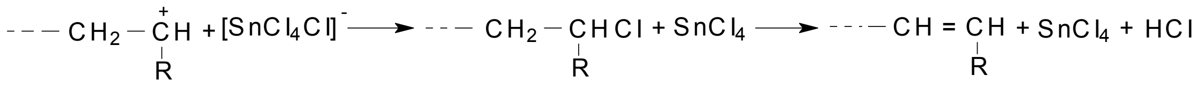
$$SnCI_4 + HCI \rightarrow [SnCI_4CI]^- + H^+$$



$$H^+ + CH_2{=}\underset{R}{CH} \longrightarrow CH_3-\overset{+}{\underset{R}{CH}}$$



$$---CH_2-\overset{+}{\underset{R}{CH}} + [SnCl_4OH]^- \longrightarrow ---CH_2-\underset{R}{CH}OH + SnCl_4 \longrightarrow ---CH=\underset{R}{CH} + SnCl_4 + H_2O$$



$$---CH_2-\overset{+}{\underset{R}{CH}} + [SnCl_4Cl]^- \longrightarrow ---CH_2-\underset{R}{CH}Cl + SnCl_4 \longrightarrow ---CH=\underset{R}{CH} + SnCl_4 + HCl$$

Kinetics of cationic polymerization:

formation of the active center: $V_{in} = K_{in}[M][K]$

chain development: $V_r = K_r[M][M_n^+]$

circuit break: $V_{uz} = K_{uz}[M_n^+$

$$\overline{P} = \frac{V_r}{V_{uz}} = \frac{K_r[M][M_n^+]}{K_{uz}[M_n^+]} \qquad \text{or}\ \overline{P} = K[M]$$

This means that the degree of polymerization of the cationic polymerization product does not depend on the catalyst concentration.

Lecture 11

Anionic polymerization.

Plan:

1. Catalysts for anionic polymerization.
2. Coordination-ionic polymerization. Ziegler-Natta catalysts.
3. Practical methods of polymerization.

Anionic polymerization

Anionic polymerization, ionic polymerization in which the terminal link of the growing chain bears a full or partial negative charge. Traditionally, anionic polymerization includes processes initiated by the combination of alkali or alkaline earth metals (or free anions).

The processes developing with the participation of transition metals are usually referred to, regardless of the nature of the polarization of the metal-carbon bond, as coordination-ionic polymerization. Most known monomers are capable of anionic polymerization, for example. unsaturated compounds containing electron-withdrawing groups in oc-positions (-CH=CH2, -C6H5, -COOR, -CN, -NO2, etc.), carbonyl compounds, oxides, thiooxides, lactones, lactams, siloxanes, and other heterocyclic compounds. Anionic polymerization is initiated by strong bases, electron donors, electric current and ionizing radiation. The compound of alkali and alkaline earth metals (eg, org. derivatives, alcoholates, amides) and other basic substances initiate anionic polymerization by the type of acid-base interaction. (attachment to the monomer M of the initiator AB or its fragment A-): Free. metals, their radical ion salts (for example, Naphthalene Naphthalene) and other strong electron donors act according to the type of redox (electron transfer to the monomer; Me-metal):

Processes of type (1) are also characteristic of electrochemical and radiation-chemical initiation. Initiation according to type (1) involves intermediate radical ion species (M-), the recombination of which leads to the formation of molecules with active sites at both ends: cases with a noticeable participation of the latter were not found. The active centers of anionic polymerization in the overwhelming majority of cases of initiation by alkali, alkaline earth metals or their compounds are derivatives of these metals.

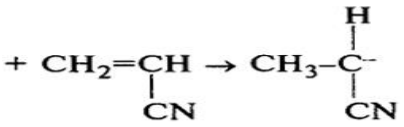
Depending on the nature of the terminal monomer unit (P), counterion (Me+), and solvent (S), active sites can exist in the form of covalent polarized molecules differing in reactivity and stereospecificity (formula II), their associates (I), ion pairs of varying degrees solvation (III, IV), free anions P (V): As a rule, the counterion is part of the active center and thus has a direct effect on chain growth events (exception is polymerization on free anions). In the limiting case, the addition of a monomer to a growing chain may be preceded by the formation of a coordination complex with a counterion (coordination ionic mechanism). This creates great opportunities for directed influence on the polymerization and properties of the resulting polymers, than in the case of processes involving "free" particles (free radicals, anions and cations). For anionic polymerization is characteristic, as a rule, refers. stability of active centers. In some cases, eg. in the anionic polymerization of nonpolar monomers in hydrocarbon solvents, the overall process includes practically only the stages of chain initiation and growth (chain termination and transfer reactions are absent or proceed at very low rates).

In this case, the so-called. living polymers, the end groups of which retain the ability to add a monomer or other reagents even after polymerization is completed. Such polymers are a convenient object both for studying the mechanism of anionic polymerization and for solving various synthetic problems: obtaining polymers with a given MWD, incl. practically monodisperse; synthesis of polymers and oligomers with terminal functional groups capable of further transformation of polycondensation or polymerization type, as well as block copolymers, graft copolymers and various polymers with controlled branching type, etc.

Anionic polymerization of monomers with polar functional groups is a more complex process, accompanied by the deactivation of active sites upon interaction with the functional groups of the monomer and polymer. The activation energy of side reactions (as well as chain transfer to the solvent in the case of substances with a mobile H atom, eg toluene), as a rule, is higher than the activation energy of chain growth; therefore, lowering the polymerization temperature usually contributes to the suppression of side reactions. The rate of anionic polymerization, especially at moderate temperatures, is in most cases much higher than the rate of radical polymerization.

This is usually associated with a higher effective concentration of active particles (in the limit, it can be equal to the initial concentration of the initiator). The intrinsic reactivity of various forms of active sites varies over a very wide range even for the same monomer. For example, for the anionic polymerization of styrene at 30 °C, the order of magnitude of abs. the chain growth rate constant (in l/mol*s) during the transition along the equilibria (2) changes from 10-1 (lithium associates, II) to 105 (free anions, V).

Anionic, or carbanionic, polymerization proceeds with the formation of a carbanion, a compound with a trivalent carbon atom bearing a negative charge. Anionic polymerization proceeds in the presence of electron donors - catalysts of the second class:

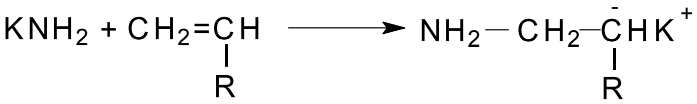


$$+\ CH_2{=}\underset{\substack{|\\ CN}}{CH} \rightarrow CH_3{-}\overset{\substack{H\\ |}}{\underset{\substack{|\\ CN}}{C}}{}^{-}$$

1) anion formation
    2Na + 2NH3 = 2Na+ + 2NH- + H2,
2) monomer activation
NH2 + CH2=CHCN → NH2-CH2-CHCN.

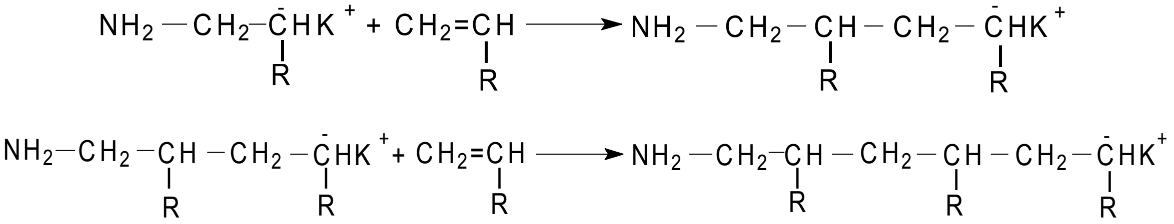
Mechanism of anionic polymerization

Formation of the active center:



$$KNH_2 + CH_2{=}\underset{R}{CH} \longrightarrow NH_2-CH_2-\underset{R}{\overset{-}{C}}HK^+$$

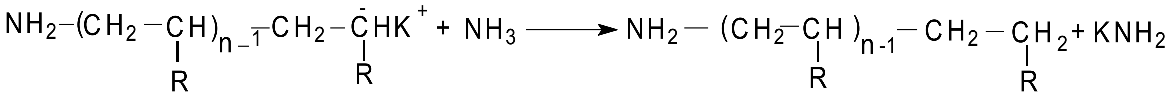
Chain development:



$$NH_2-CH_2-\underset{R}{\overset{-}{C}}HK^+ + CH_2{=}\underset{R}{CH} \longrightarrow NH_2-CH_2-\underset{R}{CH}-CH_2-\underset{R}{\overset{-}{C}}HK^+$$

$$NH_2-CH_2-\underset{R}{CH}-CH_2-\underset{R}{\overset{-}{C}}HK^+ + CH_2{=}\underset{R}{CH} \longrightarrow NH_2-CH_2-\underset{R}{CH}-CH_2-\underset{R}{CH}-CH_2-\underset{R}{\overset{-}{C}}HK^+$$

Circuit Break:

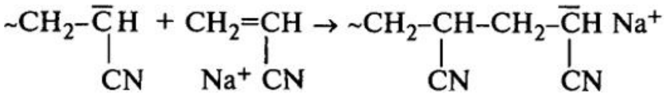


$$NH_2-(CH_2-\underset{R}{CH})_{n-1}-CH_2-\underset{R}{\overset{-}{C}}HK^+ + NH_3 \longrightarrow NH_2-(CH_2-\underset{R}{CH})_{n-1}-CH_2-\underset{R}{CH_2} + KNH_2$$

In anionic polymerization, the monomer and catalyst must be very pure, otherwise the decomposition reaction will be accelerated. It is also necessary to carry out the reaction at low temperatures. At high temperatures, radical polymerization can occur.

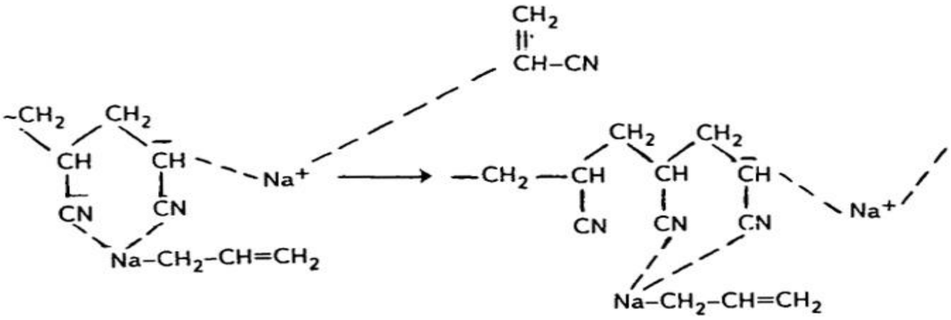
Ion-coordination polymerization. Chain growth during ion-coordination polymerization can take place:

1) as two-site coordination polymerization



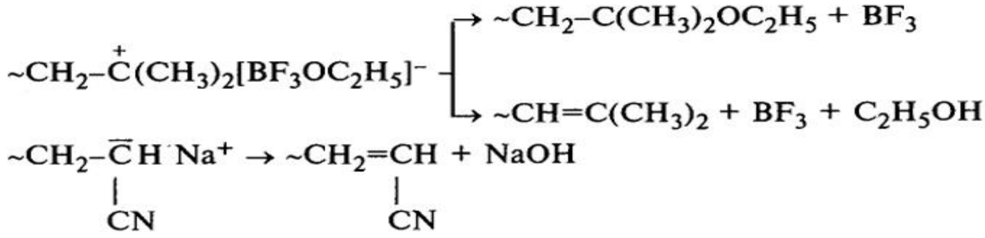
$$\sim CH_2-\underset{CN}{\overset{-}{C}H} + \underset{Na^+\ CN}{CH_2{=}CH} \rightarrow \sim CH_2-\underset{CN}{CH}-CH_2-\underset{CN}{\overset{-}{C}H}\ Na^+$$

2) as a multicenter coordination polymerization (for example, with an alfin catalyst)



The formation of stereoregular polymers during ion-coordination polymerization is possible when the process is carried out at low and even at elevated temperatures (30-70°C). With an increase in the polarity of the medium, the rate of the process and the average degree of polymerization of the synthesized product increase.

Chain termination is caused by the following reactions:



$$\sim CH_2-\overset{+}{C}(CH_3)_2[BF_3OC_2H_5]^- \rightarrow \begin{cases} \sim CH_2-C(CH_3)_2OC_2H_5 + BF_3 \\ \sim CH=C(CH_3)_2 + BF_3 + C_2H_5OH \end{cases}$$

$$\sim CH_2-\underset{CN}{\bar{C}H}\,Na^+ \rightarrow \sim CH_2=\underset{CN}{CH} + NaOH$$

The general kinetic picture of anionic polymerization is significantly complicated by the multiplicity of forms of existence of active centers mentioned above. In addition to those indicated in equations (2), more complex formations also play a role in a number of processes, for example. ionic tees like P-, Me+, P-. Therefore, even in the case of living polymers at a fast stage of initiation, when the total concentration of growing chains is equal to the initial concentration of the initiator (c0), the total rate of chain growth p-tion (Vp) is by no means always described by a simple equation: Vp = kpc0 [Ml, where kp is reaction rate constant. More complex dependences of a general form are often observed: (ci* and kpi|- concentration and growth rate constant of the i-th active center), taking into account the contribution of decomp. forms of active centers; in this case, the total order of the reaction according to the initiator varies from 1 to 0, and the monomer order is equal in most cases to 1. Naib. important special cases of the equation: (growth on the monomeric form of active centers at a concentration dominated by low-active n-mer associates; Cass-association constant) and (simultaneously growth on free ions and ion pairs at a concentration of the latter; Kdiss is the dissociation constant of active centers into ions).

For strict interpretation of kinetic data and calculation of abs. values of elementary constants, it is necessary to independently determine Cass, Kdisc and constants of other type equilibria.

In some cases, this can be done using spectral, conductometric. and other measurements, however, in general, anionic polymerization is quantitatively much less studied than, for example, radical polymerization. The participation of the counterion in the events of chain growth makes it possible to influence the microstructure of the polymer, up to the formation, in some cases, of stereoregular and optically active polymers. In naib. the degree of orienting effect of the counterion is manifested in the hydrocarbon medium, where in the presence of Li, at most. stereospecific from alkali metals, 1,4-polydienes are formed (with a predominance of the cis structure in the case of isoprene or with an equal content of cis and trans structures in the case of butadiene) and isotactic polymethyl methacrylate.

Among schel.-earth. metals the formation of cis-1,4-polydienes and isotactic. polymethyl methacrylate in max. degree contributes to VA. Electron-donor comp., saturating coordination. sphere counterion, favor 1,2(3,4)-addition of dienes and the formation of syndiotactic. polymethyl methacrylate. In industry, anionic polymerization is used by Ch. arr. for the synthesis of elastomeric materials (continuous solution polymerization, mainly on lithium initiators) - 1,4-

and 1,2-polybutadiene, statistical. butadiene-styrene copolymer, styrene-butadiene thermoplastic elastomer; the production volume of these polymers is approx. 1 million tons/year. Anionic polymerization methods are also used to synthesize butadiene oligomers with terminal functional groups, polycaproamide, polyethylene oxide, polyformaldehyde, polysiloxanes, etc. The main advantages of anionic polymerization are ease of control, the possibility of obtaining almost all of the listed homo- and copolymers of butadiene on the same equipment with minimal changes in technology. process, the presence of long-lived active sites, high purity of the products obtained. Systematic. the study of anionic polymerization of unsaturated compounds began in the 1920s. 20th century (S. V. Lebedev, K. Ziegler). Work on the theory of anionic polymerization and its practical implementation began to develop especially intensively from ser. 50s, when the ability of Li to cause the formation of cis-1,4-polyisoprene, similar in structure and properties to NC, was discovered, and the synthetic possibilities of living polymers were fully realized. the possibility of obtaining almost all of the listed homo- and copolymers of butadiene on the same equipment with minimal changes in technology. process, the presence of long-lived active sites, high purity of the products obtained. Systematic. the study of anionic polymerization of unsaturated compounds began in the 1920s. 20th century (S. V. Lebedev, K. Ziegler). Work on the theory of anionic polymerization and its practical implementation began to develop especially intensively from ser. 50s, when the ability of Li to cause the formation of cis-1,4-polyisoprene, similar in structure and properties to NC, was discovered, and the synthetic possibilities of living polymers were fully realized. the possibility of obtaining almost all of the listed homo- and copolymers of butadiene on the same equipment with minimal changes in technology. process, the presence of long-lived active sites, high purity of the products obtained. Systematic. the study of anionic polymerization of unsaturated compounds began in the 1920s. 20th century (S. V. Lebedev, K. Ziegler). Work on the theory of anionic polymerization and its practical implementation began to develop especially intensively from ser. 50s, when the ability of Li to cause the formation of cis-1,4-polyisoprene, similar in structure and properties to NC, was discovered, and the synthetic possibilities of living polymers were fully realized. the study of anionic polymerization of unsaturated compounds began in the 1920s. 20th century (S. V. Lebedev, K. Ziegler). Work on the theory of anionic polymerization and its practical implementation began to develop especially intensively from ser. 50s, when the ability of Li to cause the formation of cis-1,4-polyisoprene, similar in structure and properties to NC, was discovered, and the synthetic possibilities of living polymers were fully realized. the study of anionic polymerization of unsaturated compounds began in the 1920s. 20th century (S. V. Lebedev, K. Ziegler). Work on the theory of anionic polymerization and its practical implementation began to develop especially intensively from ser. 50s, when the ability of Li to cause the formation of cis-1,4-polyisoprene, similar in structure and properties to NC, was discovered, and the synthetic possibilities of living polymers were fully realized.

Lecture 12

Plan:

1. Types of polycondensation reaction.
2. Direction of polycondensation.
3. Effect of temperature on polycondensation. equilibrium polycondensation.

Polycondensation- synthesis processpolymers from polyfunctional (most often bifunctional) compounds, usually accompanied by the release of low molecular weight by-products (water,alcohols etc.) during the interaction of functional groups.

$$NH_2-(CH_2)_6-COOH + NH_2-(CH_2)_6-COOH \rightleftarrows$$

$$\rightleftarrows NH_2-(CH_2)_6-CO-NH-(CH_2)_6-COOH + H_2O$$

$$NH_2-(CH_2)_6-CO-NH-(CH_2)_6-COOH + NH_2-(CH_2)_6-COOH \rightleftarrows$$

$$\rightleftarrows NH_2-(CH_2)_6-CO-NH-(CH_2)_6-CO-NH-(CH_2)_6-COOH + H_2O$$

$$H\text{-}[\text{-}NH\text{-}(CH2)6 - CO\text{-}]n\text{-}OH$$

The molecular weight of the polymer formed in the process of polycondensation depends on the ratio of the initial components, the reaction conditions.

They can enter into polycondensation reactions as onemonomer with two different functional groups: for example, the synthesis of poly-ε-caproamide (nylon-6,capron) fromε-aminocaproic acid, and two monomers bearing different functional groups, for example, the synthesis of nylon-66 by polycondensation of adipic acid andhexamethylenediamine; in this case, polymers of a linear structure are formed (linear polycondensation.

If the monomer (or monomers) carry more than two functional groups, cross-linked polymers with a three-dimensional network structure (three-dimensional polycondensation) are formed. In order to obtain such polymers, “cross-linking” polyfunctional components are often added to a mixture of monomers.

The reactions of polymer synthesis from cyclic monomers by the mechanism of ring opening stand apart - addition, for example, synthesisnylon-6 ofcaprolactam(cyclicamide ε-aminocaproic acid); despite the fact that the isolation of a low molecular weight fragment does not occur, such reactions are more often referred to as polycondensation. Main industrial groupspolymerssynthesized by polycondensation:Linearpolymers,Polyamides,Polyurethanes,Polycarbonates,Polyesters,Polysiloxanes, Meshpolymers, Alkyd resins, Melamine-aldehyde resins, Urea-aldehyde resins, Phenol-aldehyde resins.

Almost allbiopolymers (squirrels,DNA AndRNA,cellulose,chitin etc.) are synthesized in living organisms by polycondensation with the participation of the corresponding complexesenzymes.

Heteropolycondensation:

$HOOC - (CH_2)_4 - COOH \quad + \quad H_2N - (CH_2)_6 - NH_2 \rightarrow$

adipin acid **geksametilendiamin**

$\rightarrow HOOC – (CH_2)_4 – CO – HN – (CH_2)_6 – NH_2 + H_2O$

nylon

Homopolycondensation:

$nH_2N - (CH_2)_5 - COOH \rightarrow - HN - (CH_2)_5 - CO -$

Lecture 13

Factors affecting the molecular weight during polycondensation

Plan:

1. Carothers equation.
2. Rules of non-equivalence of Korshak.
3. Destructive reactions during polycondensation.
4. Staged (migration) polymerization.
5. Transformation of cyclic compounds into linear polymers.

Carothers equation

$$\overline{f} = \frac{\sum n_i f_i}{\sum n_i}$$

Where, $\overline{f}$ -average values of functional groups.

$$p = \frac{2(N_0 - N)}{N_0 \overline{f}} = \frac{2N_0}{N_0 \overline{f}} - \frac{2N}{N_0 \overline{f}} = \frac{2}{\overline{f}} - \frac{2}{\overline{f}} \cdot \frac{N}{N_0}$$

$$N_0 = \overline{x}N \quad \text{yoki} \quad \frac{N}{N_0} = \frac{1}{\overline{x}}$$

$$p = \frac{2}{\overline{f}} - \frac{2}{\overline{x}\,\overline{f}} \qquad \overline{x} = \frac{2}{2 - p\overline{f}}$$

1. Monomers had one functional group, let the reaction proceed completely ($\overline{f} = 1$ And $p = 1$) and substitute the values $\overline{f}$ and R into the equation $\overline{x} = \frac{2}{2 - p\overline{f}} \Rightarrow \overline{x} = \frac{2}{2 - 1 \cdot 1} = 2$ will.

This means that the monomer contains one functional group, no high molecular weight compound is formed even if the reaction ends in 100% yield.

2. Let the reaction proceed between bifunctional monomers of equimolecular size:

HO - R - OH + HOOC - R' - COOH

$$\overline{f} = \frac{2+2}{2} = 2 \qquad p = \frac{2}{\overline{f}} - \frac{2}{\overline{x}\,\overline{f}} = 1 - \frac{1}{\overline{x}} \qquad \overline{x} = \frac{1}{1-p}$$

To obtain a product with a degree of polymerization of 10, the reaction must be 90% (P = 0.9). The reaction occurs only at a yield of 99.8% ($p = 1 - \frac{1}{500}$). It can be concluded that reversible polycondensation, when it practically goes to the end of the reaction, then a high-molecular compound is formed.

Thus, even if an infinite number of monomeric residues are involved in the formation of macromolecules, theoretically all functional groups cannot be affected.

In practice, heteropolycondensation reactions are often carried out in the presence of two different monomers, each containing two functional groups of the same type. In such cases, the most favorable conditions are created when each individual group corresponds to a different type of group, i.e. when the monomers are obtained in equivalent quantities. Only in this way are high molecular weight products formed.

Lecture 14
Methods for obtaining polymers in industry.

Plan:

1. Polymerization in solution, block and solid phase.
2. Emulsion and suspension polymerization.
3. Polycondensation in solution, mass and interfacial medium.

Radical polymerization is carried out in block (mass), solution, emulsion, suspension and gas phase. In this case, the process can proceed under homogeneous or heterogeneous conditions. In addition, the phase state of the initial reaction mixture may also change during polymerization.

1. Polymerization in block (in bulk)

The polymerization is carried out without a solvent. Due to the high exothermicity, the polymerization process is difficult to control. In the course of the reaction, the viscosity increases and heat removal becomes more difficult, as a result of which local overheating occurs, leading to the destruction of the polymer and its inhomogeneity in molecular weight. The advantage of bulk polymerization is the possibility of obtaining a polymer in the form of a vessel in which the process is carried out without any additional processing.

2. Solution polymerization

Unlike polymerization in the block, in this case there are no local overheatings, since the heat of reaction is removed by the solvent, which also acts as a diluent. The viscosity of the reaction system decreases, which facilitates its mixing.

However, the role (share) of chain transfer reactions increases, which leads to a decrease in the molecular weight of the polymer. In addition, the polymer may be contaminated with solvent residues, which cannot always be removed from the polymer.

There are two ways to carry out solution polymerization.

a) A solvent is used in which both the monomer and the polymer dissolve. The resulting polymer is used directly in solution or isolated by precipitation or evaporation of the solvent.

b) The solvent used for polymerization dissolves the monomer but does not dissolve the polymer. The polymer precipitates out in solid form as it forms and can be separated by filtration.

3. Suspension polymerization (bead or pellet)

Widely used for the synthesis of polymers. In this case, the monomer is dispersed VH_2Oin the form of small drops. The stability of the dispersion is achieved by mechanical mixing and the introduction of special additives - stabilizers into the reaction system. The polymerization process is carried out in monomer drops, which can be considered as block polymerization microreactors. Monomer soluble initiators are used.

The advantage of this process is good heat removal, the disadvantage is the possibility of contamination of the polymer with stabilizer residues.

4. Emulsion polymerization (emulsion polymerization)

In emulsion polymerization, the dispersion medium is water. Various soaps are used as emulsifiers. For initiation, water-soluble initiators are most often used, redox systems.

Polymerization can proceed in a molecular solution of the monomer in H_2O, on the interface a drop of monomer - H_2O, on the surface or inside the soap micelles, on the surface or inside the resulting polymer particles swollen in the polymer.

The advantages of the process are: high speed, formation of a polymer of large molecular weight, ease of heat removal. However, as a result of emulsion polymerization, a large amount of wastewater is generated that requires special treatment. It is also necessary to remove emulsifier residues from the polymer.

5. Gas-phase polymerization

In gas phase polymerization, the monomer (eg ethylene) is in the gaseous state. can be used as initiators. O_2 and peroxides. The process proceeds at high p.

Lecture 15

Physical chemistry of polymers and their solutions. Configuration isomerism and configuration of macromolecules.

Plan:

1. Configuration isomerism and configuration of macromolecules.
2. Conformational isomerism and conformation of macromolecules.
3. Possibilities of internal rotations and flexibility of a macromolecule.
4. The concept of a statistical segment. Kuhn segment.
5. Kinetic and thermodynamic flexibility and methods for their determination.

The most general idea of the dissolution process can be obtained from a thermodynamic consideration. If two substances (two phases) are mixed under known thermodynamic conditions (temperature, pressure), then the energy result of such a process can be expressed by the second law of thermodynamics.

As is known, the principle of minimum energy as applied to the second law of thermodynamics indicates that spontaneous mixing of the components of two or more phases will occur only when their total free energy decreases. It follows from this that isothermal mixing requires either a sharp decrease in internal energy, which overlaps the increase in entropy, or an increase in entropy that exceeds the increase in internal energy, or a simultaneous decrease in internal energy and an increase in entropy. In addition, dissolution may begin or improve with increasing temperature. When mixed, the energy state of each component changes.

The modern thermodynamic theory of polymer solutions, which was initiated by the works of Flory and Huggins, has been developed quite fully and rigorously only in relation to systems that include nonpolar components.

This theory is based on the so-called lattice solution model, in which each equivalent cell can be occupied either by a solvent molecule - and a low-molecular component, or by a unit of a polymer molecule (segment) equal in volume to it. The essential difference between the lattice model of a polymer solution and the model of a mixture of two low molecular weight liquids, the molecules of which occupy the same volumes, is the requirement that the units of the macromolecule be located in neighboring cells, and not in random places of the entire volume.

To calculate the entropy of mixing, it is necessary to subtract the entropy of disorientation of the ordered polymer from the entropy of the solution. This expression for the nonideal entropy of mixing differs from the usual expression for the ideal entropy of mixing, which characterizes the mutual dissolution of two low molecular weight liquids, in that it includes volume fractions instead of mole fractions.

It is easy to conclude that when a polymer substance is added to the same solvent, the entropy of mixing will be less than when the same volume of a low molecular weight liquid is added. When obtaining the expression for the configurational entropy based on the lattice model, it was assumed that the arrangement of molecules in the lattice of the solution is completely random, i.e., some cell of the solution can be filled with equal probability either by a solvent molecule or by a segment of the polymer chain, which are in the vicinity of this cell . At the same time, in order to change the enthalpy during mixing, it was necessary to take into account the change in potential energy during the interaction of heterogeneous molecules, i.e., to recognize the fact of the unequal energy state of various molecules in solution. Naturally, in this case, the equiprobability of getting any solvent molecule into a lattice cell, located near the polymer chain is excluded. This is one of the reasons why the Flory-Huggins theory is applicable only to non-polar polymer-organic solvent systems, where solvation effects are relatively small.

The Flory-Huggins theory brings us to the notion of "good" and "bad" solvents, and here one involuntarily recallsseries "Bad", or Misfits; To purely empirical ideas about the "quality" of a solvent, the thermodynamic theory of solutions is able to give a quantitative interpretation.

The stability of the solution is determined by the ratio 0/7, on which the value and sign of A depend. The value of 0 in the literature is usually called the "Flory temperature". As the temperature of the solution decreases from 1 to 6, the heat of mixing, which is determined by the change in the energy of intermolecular interaction in the solution, is exactly compensated by the configurational entropy. We encountered a similar phenomenon when considering hydration processes: large negative values of the change in the potential energy of water-ion interaction did not necessarily lead to positive hydration due to the need to compensate for the change in entropy.

The Flory temperature can be set for any polymer-solvent pair by changing the slope of the curves of the dependence of osmotic pressure, viscosity, light scattering and other parameters on the polymer concentration at different temperatures, and the Flory temperature corresponds to an isotherm expressed by a straight line parallel to the concentration axis. Then, a bad solvent should be understood as such a solvent, which, under the given dissolution conditions, has a lower temperature. In this case, the attractive forces between the polymer molecules exceed the attractive forces between the polymer and solvent molecules, so that dissolution does not occur, and if the solution already exists, then the solute molecules are associated.

So in theory all solvents should be good or bad depending on what the temperature of the solution is. Some solvents always behave as good only because the freezing point of the solution is above 0. Non-solvents (consistently bad solvents) boil below the Flory point, and the solubility temperature range cannot be realized.

Consequently, the solution as a homogeneous system is far from invariant with respect to temperature. True, the process of phase separation can be slowed down, and it is sometimes difficult to establish whether this process occurs at all, especially in aqueous systems. Thus, when a PVA solution obtained at 70°C is cooled to room temperature, the viscosity sharply increases, but phase separation is not observed. Only with prolonged standing, the solution begins to opalescent and becomes cloudy, which indicates the process of stratification. Such a "solution" may not delaminate for a long time, but all its properties (viscosity, surface tension, etc.) differ from the properties of a true solution.

The basic equation of the Flory-Huggins theory indicates that when a polymer is mixed with a solvent, the enthalpy change is always positive. Therefore, the Flory-Haggis theory is unable to substantiate two fairly common phenomena: the experimentally observed negative value of the heat of mixing of polymers with solvents, as well as the fact that for the same polymer-solvent system, phase separation can occur not only at low, but also at high temperatures. Let us try to analyze how useful thermodynamic consideration can be for evaluating real systems.

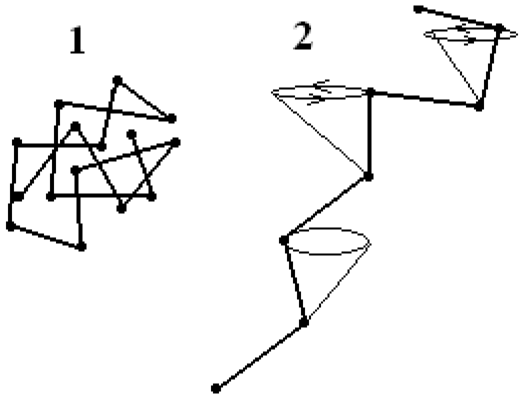
The Flory-Huggins equation is valid for some polymer systems when the mixing process becomes purely entropic. The concept of nonideal entropy used in the lattice model of a Flory-Huggins polymer solution is only the first approximation to a quantitative description of structural changes when a polymer is mixed with a low molecular weight liquid. The fact that a polymer molecule containing a certain (moreover, rather large) number of kinetic units exhibits the properties of a collective system plays an enormous role here.

Flexibility of polymers

The flexibility of macromolecules is one of the most important characteristics of a polymer, which determines its main macroscopic properties. The flexibility of macromolecules is the ability of polymer chains to change their conformation as a result of intramolecular thermal movement of units (thermodynamic flexibility) or under the action of external mechanical forces (kinetic flexibility). The flexibility of macromolecules is due to the fact that the monomeric links of the chain during thermal motion or under external force influences rotate around single (s-) bonds.

The concept of internal rotation of polymer macromolecules was first introduced by Kuhn, Mark and Guth. When the links rotate, the macromolecule changes its shape. Forms of a macromolecule that pass into each other without breaking chemical bonds are called conformations. Many types of conformations of macromolecules are known: coil conformation, elongated rigid rod conformation, helix conformation, globule conformation (the most compact), folded (lamellar) conformation (usually in crystalline polymers), etc.

Consider one isolated polymer chain, the carbon atoms in which are linked only by s-bonds. Let us assume that the bond angles in such a chain are not fixed and the rotation around s-bonds is free. Such a model chain is called freely articulated. The links of a freely articulated chain can occupy arbitrary positions in space, regardless of the position of neighboring links. Such a chain can take any conformation, i.e. is extremely flexible.



Rice. Loosely articulated chain (1) and chain with fixed bond angles (2)

In real polymer chains, the bond angles have a well-defined value, and the rotation of the units occurs without changing them. Therefore, in a real chain, the links are not arranged arbitrarily: the position of each subsequent link turns out to be dependent on the position of the previous one. Even if we assume the free rotation of the links, then such a chain can take a smaller number of conformations than a freely articulated one. But it is able to bend strongly due to the rotation of the links. Molecules in which rather intense rotations of links around s-bonds are observed are called flexible chain, and polymers with weak rotations are called rigid chains. There are thermodynamic and kinetic flexibility of macromolecules

Thermodynamic flexibility (equilibrium flexibility) –the ability of macromolecules to change their conformations as a result of intramolecular thermal motion of units. Let us imagine a situation where one group of atoms of a polymer chain has received a certain momentum as a result of the thermal motion of the links. An absolutely rigid molecule would have to move entirely to a new position in space under the influence of this impulse. In a flexible macromolecule, only a certain part of it moves. Impulses of different magnitudes applied to different sections of the molecule will lead to the movement of sections of various sizes. An average segment of a macromolecule moving as a whole in an elementary act of thermal motion is called a segment (statistical segment of a macromolecule or Kuhn's statistical element). The stiffer the chain, i.e. the greater the rotational activation barrier DU, the larger segment of the chain moves in the elementary act of thermal motion, i.e. the larger the segment. Thus, the segment size can serve as a measure of the thermodynamic flexibility of macromolecules. A real molecule can be represented as consisting of N segments, each of length A:

$$L = N \times A$$

where L is the chain length. For a freely articulated chain, A is the length of the link, and for an extremely rigid macromolecule, A = L.

The idea of a segment is not purely formal. It turned out that when measuring the molar mass of the polymer by any physicochemical method based on the colligative property (ebullioscopically, cryoscopically, osmometry, etc.), it turns out that it is less than the true molar mass measured, for example, by the viscometric method, and equal to the molar mass of the segment. This means that macromolecules in solutions behave not as a single entity, but as a collection of small molecules with a length equal to the length of segment A.

As another estimate of thermodynamic flexibility, the ratio of the root-mean-square dimensions of a macromolecule coiled into a statistical coil to the dimensions that the same molecule would have with absolutely free rotation of the links can serve.

Kinetic flexibility of macromoleculesis the ability of macromolecules to change their conformations as a result of external mechanical forces. Depending on the ratio of the energy of these external influences and the potential barrier to rotation of the DU units, the polymer chain can unfold to some extent; exhibit kinetic flexibility.

By analogy with thermodynamic flexibility, the length of the kinetic segment can act as a measure of kinetic flexibility. Indeed, if as a result of an external influence (for example, we pulled the ends of a polymer tape) one group of atoms of the polymer chain receives a certain momentum, then in the case of a flexible macromolecule, only a certain section of it will move. Impulses of different magnitudes applied to different sections of the molecule will lead to the movement of sections of various sizes. A kinetic segment is an average segment of a macromolecule that moves as a whole in an elementary act of external influence. The shorter the segment, the higher the kinetic flexibility of the macromolecule.

Most often, as a measure of kinetic flexibility, it is customary to consider the glass transition temperature - the temperature interval for the transition of a polymer from a glassy to a highly elastic state. The higher the glass transition temperature of a polymer, the lower the kinetic flexibility of its macromolecules.

A universal and widespread method for determining Tst and Tm, as well as studying the deformation properties of polymers, is the thermomechanical method. The method consists in measuring the dependence of deformation e on temperature T, a graphical representation of this dependence is called a thermomechanical curve.

For amorphous linear polymers of high molecular weight, the thermomechanical curve has three segments corresponding to three physical states.

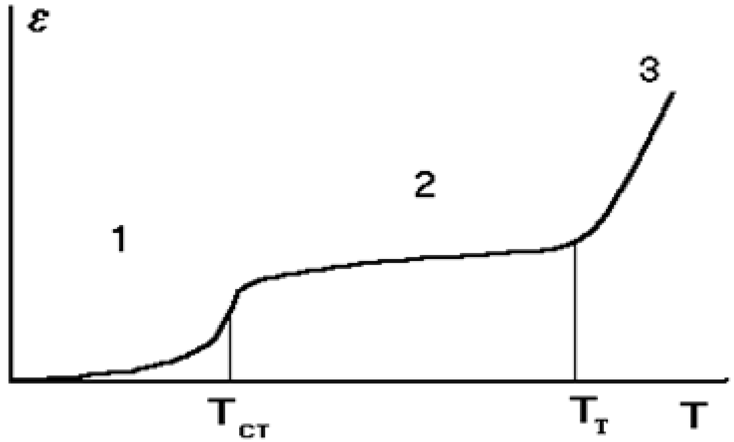


Fig. Thermomechanical curve of a linear amorphous polymer

The first section (1) corresponds to the glassy state, which is characterized by small deformations, the second (2) corresponds to the highly elastic state with large reversible deformations. These deformations are superimposed (under prolonged action of the load) by the deformation of the flow, which increases with increasing temperature. At sufficiently high temperatures, the movements of the chains as a whole are so facilitated that the true flow of the polymer sets in. The polymer goes into a viscous state. This transition is accompanied by a sharp increase in deformation (region 3).

The temperatures Tst and Tm correspond to the average values of the temperature intervals at which the transition from one physical state of the polymer to another takes place.

Depending on the free volume, the polymer substance is in one of the physical states - glassy, highly elastic, viscous. Transitions from one state to another occur without the release or absorption of heat. The transition temperatures are called glass transition temperatures Tsti flow Tm.

Below T, the intermolecular attraction excludes rotations around the bonds, but it is not strong enough to exclude such rotations under the action of an external load.

Polymers under load exhibit low stiffness and creep. The low stiffness is the result of reversible rotations around the bonds and distortion of the angles between the bonds under a short-term load. Under prolonged loading, the deformation is essentially the result of irreversible rotation around the bonds and is called forced elastic deformation. Elongated molecules represent one of the varieties of nonequilibrium structures.

The supramolecular structures of thermoplastics below Tst depend on the conditions of processing and cooling of the material and usually turn out to be nonequilibrium. Preservation of non-equilibrium structures in products is a characteristic feature of thermoplastics. Obtaining one - or biaxial orientation in polymer films is used to increase strength; oriented polymer fibers form an important group of high strength fibers.

The transition of non-equilibrium structures to equilibrium ones is accompanied by warping and shrinkage of products during operation. To reduce this shortcoming, thermal stabilization is used - annealing - at temperatures exceeding the maximum operating temperatures.

Supramolecular structures in which tensile stresses from an external load act along valence bonds are characterized by high rigidity. Similar structures are formed after a very large drawing of polymer fibers. The elementary structural unit of a fiber, a fibril, contains alternating crystalline and amorphous sections. In the amorphous regions, the molecules are stretched to the limit. It is these areas that are loaded when the fiber is stretched, as a result of which the elastic modulus (E) is very large. For ordinary polyethylene with an amorphous-crystalline structure, E \u003d 120 ... 260 MPa, for polypropylene E \u003d 160 ... 320 MPa. The copolymer of ethylene and propylene at a monomer ratio of 1:1 does not crystallize and at a temperature of 20-25 ° C is rubber, its modulus (at a stretch of 300%) is only 9-15 MPa.

VI-semester
Lecture 16
Supramolecular structure of polymers
Plan:

1. Amorphous and crystalline polymers.
2. Features of the physical properties of polymers.
3. Relaxation properties. Phase properties of polymers.
4. Factors affecting the crystallization of polymers.

The limiting case of ordering of crystalline polymers is the formation of ideal crystalline bodies - single crystals, in which strictly the same relative arrangement of the atom is preserved throughout the volume. All real bodies contain more or less strict distortions in the form of so-called dislocations, defects of various types. In polymers, deviations from strict ordering can be associated both with violations of the strict regularity of the chain structure, and with the fact that the bonding of atoms into a single long chain prevents their free diffusion, which is necessary for the formation of an ideal crystal. Therefore, regions of higher and lower order always alternate in polymers. These regions cannot be separated from each other, since they contain the same chains. Therefore, these regions do not form separate phases, and the entire structure of a crystalline polymer can be considered as a defective crystal or as a complex combination of crystalline and amorphous regions of varying degrees of order. Therefore, X-ray diffraction patterns of crystalline polymers always contain, along with even ring reflections, a wide amorphous halo. Therefore, a crystalline polymer is essentially partially crystalline. As a quantitative characteristic of the degree of ordering of a partially crystalline polymer, the term degree of crystallinity is often used, which is determined based on the equation: Therefore, X-ray diffraction patterns of crystalline polymers always contain, along with even ring reflections, a wide amorphous halo. Therefore, a crystalline polymer is essentially partially crystalline. As a quantitative characteristic of the degree of ordering of a partially crystalline polymer, the term degree of crystallinity is often used, which is determined based on the equation: Therefore, X-ray diffraction patterns of crystalline polymers always contain, along with even ring reflections, a wide amorphous halo. Therefore, a crystalline polymer is essentially partially crystalline. As a quantitative characteristic of the degree of ordering of a partially crystalline polymer, the term degree of crystallinity is often used, which is determined based on the equation:

$$\mathbf{C=Ca(1-x)+Ckx}$$

where C is a measured index of some property of the polymer; Ca and Ck are the values of this indicator for a purely amorphous and purely crystalline polymer; x is the fraction of the crystalline polymer.

A complete characterization of the structure of a substance is based on a detailed description of its morphology, i.e. aggregates observed structural formations, their forms and boundaries, mutual arrangement and hierarchy. The main morphological forms of crystalline polymers include various single crystals (lamellar, fibrillar, globular) and spherulites, as well as some intermediate morphological formations.

crystallographic cells.

The simplest element of any morphological form of a crystalline polymer is a crystallographic cell, information about which is obtained on the basis of X-ray diffraction studies. It is characterized by strictly defined sizes-distances between atoms or lattice periods (parameters) a, b, c and angles α, β, γ between the planes in which these atoms lie. Cells in polymers are no different from cells formed by low molecular weight compounds.

A typical example of a crystallographic cell formed in polymers is the orthorhombic spatial unit cell of polyethylene (a=0.705 nm; b=0.493 nm; c=0.253 nm).

The density of the crystal corresponding to these dimensions is 1.0 g/cm3. Polyethylene chains, like other paraffins, enter the crystal cell in the form of a flat zigzag, in which all carbon atoms are located in the same plane. In an elementary orthorhombic polyethylene cell, the chains are located along four edges and in the middle of the cell. In contrast to polyethylene, linear chains with bulky side substituents are characterized not by a flat zigzag, but by a helical conformation of the macromolecular chains included in the crystal. One turn of the helix, depending on the nature of the polymer, can contain a different number of monomer units, so that the parameters of unit cells can vary within very wide limits.

The crystallographic cell is the primary structural element of any crystalline polymer. The different mutual arrangement of elementary cells leads to the formation of higher structural forms within the crystalline state of the substance, which determine the morphology of the crystalline polymer.

Lamellar (lamellar) single crystals.

The simplest single crystals of polymers are monocomplex flat plates (lamellas), often rhomboid in shape, 10 nm thick and with plate sides up to 1 μm in size. The axes a and b of the crystallographic cell correspond to the long and short diagonals of the rhombus, and the c axis, along which the macromolecular chains are corrected, is perpendicular to the plane of the crystal. Since the length of macromolecules is tens of thousands of angstroms, and the thickness of the crystal does not exceed 20 nm, the chain cannot fit into the crystal perpendicular to its larger plane except by turning on its surface by 1800, that is, the conformation of the polymer chain entering the crystal is characterized by the appearance of regularly repeated bends (folds). In this case, the chain is said to be in a folded conformation. The return of the chain to the crystal during the formation of a fold can occur in different ways. Thus, the folding surface can have a regular structure if the chain, after exiting the crystal, returns to it at a strictly defined distance from the point of exit. The folding surface turns out to be completely disordered if the chain leaving the plate does not return near the exit point, but at some distance from it does not return to this crystal at all, but forms long loops, free ends, and other more or less defective regions. Other intermediate cases of the structure of folding surfaces in plates are also possible. There are also polymers built from straightened chains. Single crystals with straightened chains (the so-called crystals in which the size along the c axis, coinciding with the direction of macromolecular chains, is at least 20 nm) are the most perfect forms of the polymer structure. An example is the structural forms, called "shish kebabs", which are characterized by the presence of a long fibrillar central stem formed by molecules of high molecular weight. On this rod, as on a germ, lamellae grow in the transverse direction, in which the chains are in folded conformations.

Plates are primary structural elements, the different arrangement of which leads to a huge variety of structural forms of crystalline polymers. Thus, an increase in the solution concentration leads to further development of structure formation based on lamellar crystals. In such cases, crystal structures characteristic only for polymers are formed in the form of polyhedra (they are called hedrites and axiamites) or ovals (ovoids). In appearance, such structures resemble single crystals, but much larger in size: their length reaches several millimeters, and their thickness is 1 μm.

Spherulites

In the study of many crystalline polymers by optical microscopy, structures are detected. Such spherically symmetrical formations, built from radially arranged rays diverging from the center, are called spherulites.

Spherulites are typical polycrystalline formations obtained under real conditions for molding castings, films, fibers and other polymer products based on crystallizing macromolecular compounds of almost all classes. Spherulites grow during the crystallization of polymers from melts or concentrated solutions of high viscosity. The sizes of spherulites range from a few microns to fractions of a millimeter, and in some cases they reach values of the order of a centimeter. Spherulites are built from crystalline fibrillar or lamellar structural elements (crystallites) that grow radially from one common center. Macromolecular chains in the spherulite are located perpendicular to the radius or, in any case, form an angle with it not less than 60°, that is, they are located tangentially with respect to the radius of the spherulite.

Spherulites are best distinguished when thin films or sections of polymers are examined in an optical microscope in polarized light. This is due to the fact that spherulites are characterized by anisotropy of optical properties due to the radial symmetry of their structure. Therefore, the refractive indices of light in the radial and tangential directions are different, and birefringence patterns typical of spherulites are visible in polarized light. The observed pattern is explained by the fact that the orientation of the crystallographic axes in the spherulite continuously changes along the angular coordinate. This corresponds to the same continuous change in the refractive indices with respect to the plane of polarization of the incident light. Therefore, different regions of the spherulite transmit polarized light in different ways. This leads to the appearance of a bright circular birefringent region, crossed by a dark figure in the form of a Maltese cross, the shoulders of which are parallel to the directions of extinguishing the incident light. Such spherulites are called radial. If the value of the refractive index measured in the radial direction is greater than in the tangential direction, then such a spherulite is called positive, otherwise they speak of a negative spherulite.

In addition to the radial ones, there are also ring spherulites characterized by the fact that a pronounced system of alternating dark and light rings is superimposed on the pattern of the Maltese cross.

In spherulites of the radial type, one of the axes of the crystallographic lattice retains a constant direction in all radial directions. Ring-type spherulites are built from lamellar crystals, the orientation of which continuously changes along the radius of the spherulite. Therefore, the directions of the crystallographic axes gradually rotate relative to the radius, forming right or left spirals. A change in orientation occurs in each radial direction, resulting in a pattern of alternating dark and light rings.

Spherulites are complex polycrystalline formations composed of the simplest structural forms. The presence of spherulites inevitably entails an increase in the degree of defectiveness of the crystal structure compared to that arising in the simplest structural elements. In this case, spherulites are naturally characterized by all types of defects characteristic of the simplest structural forms - local distortions of crystallographic lattices, disordered folding surfaces of macromolecular chains. In addition, in a spherulite, even after the completion of crystallization, a part of the material may remain amorphous and not enter into crystalline formations. This part of the material in one way or another (for example, by etching the polymer) can be separated from the substance, and thus, it is a truly amorphous phase. Macromolecules in such areas are predominantly in the form of globules. The simplest structural elements inside a spherulite, like themselves; spherulites are interconnected by a large number of interstructural bonds in the form of passing macromolecules, macromolecule bundles or crystallized fibrillar formations, built mainly from chains in a straightened conformation.

It follows from the foregoing that crystalline polymers contain a wide variety of structural formations of the most varied degrees of order, sizes, and shapes. The main structural elements of crystalline polymers and their characteristic dimensions are given below:

Smallest size, nm Largest size, nm
Molecule 0.2-0.5 103-105
Crystallographic cell 0.3-0.5 2.5-3.0
Crystallite 2—10 10-50
Monocrystal 100 103-104
Edrites, ovoids 10-103 103-105
Spherulites 104-106 >106

Lecture 17
Physical states of polymers.
Plan:

1. The concept of physical states

Fig. 2. Dependence of the glassy, highly elastic and viscosity-flowing state on the molecular weight of the polymer

Depending on the structure and method of preparation, polymers are in an amorphous, crystalline, or amorphous-crystalline state. Most polymers usually have an amorphous state. Only stereoregular polymers have a crystalline structure. Due to the regular structure and flexibility, macromolecules can approach each other at a fairly close distance, i.e. so that between them there will be effective intermolecular interactions, and even hydrogen bonds, which lead to ordering of the structure. The crystallization process proceeds in several stages.

At the first stage, bundles appear, associates of ordered molecules. Fibrils and spherulites are formed from packs. Fibrils are aggregates of elongated packs, and spherulites are needle-shaped formations that radiate from one center.

Single crystals are formed from fibrils and spherulites.

*Crystalline polymers*consist of a large number of crystals, between which there are areas with a disordered (amorphous) structure. Therefore, such polymers are characterized by a certain degree of crystallinity. For example, the degree of crystallinity of polyethylene can reach 80%. The most pronounced ability to form crystals in polyolefins, polyamides, polyesters.

The properties of crystalline and amorphous polymers are different.

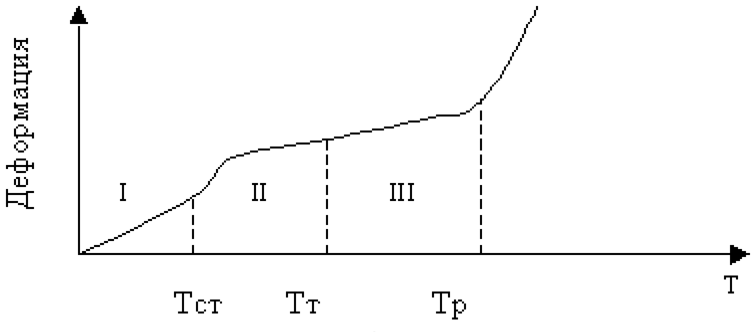
*Amorphous polymers*are characterized by a region of gradual transition from a solid to a liquid state, and crystalline ones have a certain melting point.

Amorphous polymers can be in the following state:

- glassy;
- highly elastic;
- viscous.

At low temperatures, the polymer is in a glassy state (region I), in which the polymer behaves like an elastic body (where there is no movement of either the entire molecule or individual links, but only vibrations of atoms around the equilibrium position).

With an increase in temperature, the polymer passes into a highly elastic state, where the substance is capable of significantly reversible deformations (due to the mobility of links and the flexibility of macromolecules). The movement of the links is not instantaneous, therefore, the deformations are of a relaxation nature, that is, they are characterized by the time of equilibrium establishment (highly elastic states from glass transition T to yield T - region II).



Rice. Various States of Amorphous Polymers

If the interval Tst - Tt is wide and captures ordinary temperatures, such polymers are called elastics or elastomers, rubbers.

Polymers with a narrow range of Tst - Tt, shifted in the region of elevated temperatures, are called plastics (plastomers), they are in a glassy state at ordinary temperatures.

At temperatures above T, it is fluid. (region III) the polymer passes into a viscous state. Increasing the temperature above Tp leads to destruction, destruction of the polymer. A substance in a viscous state under the action of shear stress flows like a viscous liquid, and the deformation of the polymer is irreversible.

The viscous-flowing state is characterized by the mobility of both links and the entire molecule (during the flow of polymers, macromolecules straighten out, approach each other, the polymer becomes rigid, and mechanical glass transition begins).

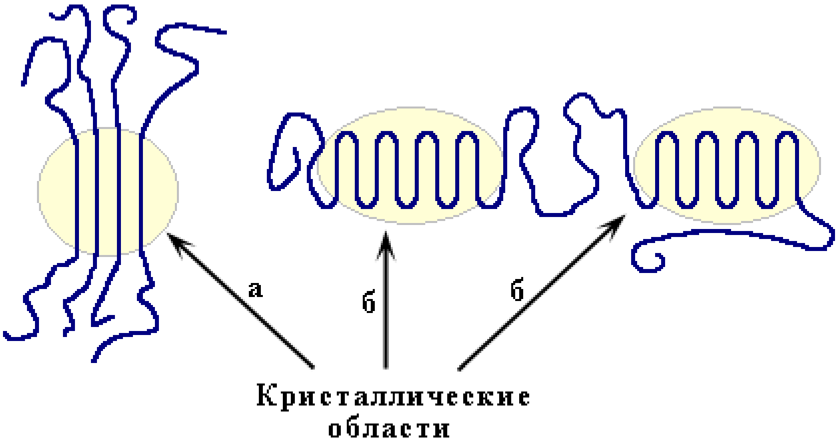
The polymer can be transferred to a viscous state by adding solvents or plasticizers - in the manufacture of varnishes, paints and other products

Depending on the structure and external conditions, polymers can be in amorphous or crystalline states.

- The amorphous state of the polymer is characterized by the lack of order in the arrangement of macromolecules.
- The crystalline state is possible only for stereoregular polymers. Moreover, it differs significantly from the ordered crystalline state of low molecular weight substances. Crystalline polymers are characterized by only partial ordering of macromolecules, since the crystallization process is hindered by the long chain structure of macromolecules.

The crystallinity of polymers is understood as an ordered arrangement of some individual sections of chain macromolecules.

The same macromolecule can pass through crystalline and amorphous regions.



а) фибриллярная структура; б) складчатая структура.

The fibrillar structure of the crystalline regions is characteristic of rigid-chain polymers, while the folded structure is characteristic of flexible-chain polymers.

In a crystalline polymer, there are always amorphous regions, and one can only speak about the degree of its crystallinity. The degree of crystallinity can vary in the same polymer depending on external conditions. For example, when a polymer sample is stretched, the mutual orientation of macromolecules occurs, which contributes to their ordered parallel arrangement, and the crystallinity of the polymer increases. This property of polymers is used when drawing fibers to give them increased strength.

For amorphous polymers, depending on the temperature (and the magnitude of mechanical stress), three physical (deformation) states are possible: glassy, highly elastic, and viscous. The practical application of polymers is determined by which of these states the given polymer is in at the temperature of its use.

Glassy polymers are characterized by relatively small elastic (reversible) deformations (1-10%). Moreover, polymer glasses differ in increased strength from low-molecular glassy bodies, which are destroyed during deformation already by 0.1-1%. Polymers in the glassy state are used in the production of plastics.

Highly elastic polymers are capable of reversibly deforming by hundreds of percent. All rubbers are in a highly elastic state under operating conditions. This state is typical only for polymers.

In the viscous state, the polymer behaves like a very viscous liquid, which, under the action of a force, exhibits an irreversible deformation (flow deformation). This state is usually realized at elevated temperatures and is used to process polymers into products.

Lecture 18

Polymer strength

Plan:

1. Mechanical properties of crystalline and amorphous polymers.
2. Strength of polymers and operational properties.
3. Plasticization of polymers. Rules of Kargin and Zhurkov. plasticization mechanism.
4. Plasticization of polymers with other polymers.

Polymers have low density (from 920 for polyethylene to 1700, rarely 2300 kg/m3 for polytetrafluoroethylene) and high mechanical properties.

The ultimate strength of polymers in tension ranges from 10 to 60 MPa and higher, and in compression, the ultimate strength ranges from 20 to 180–200 MPa. Individual polymers and materials based on them have a strength that exceeds the strength of wood, stone, ceramics, some metals and alloys.

Mechanical properties of polymers

Mechanical properties determine the degree of change in the structure, size, shape of the body when mechanical forces act on it. All mechanical properties of polymeric materials are classified into deformation and strength properties.

The ability to large reversible deformations is a characteristic property of polymeric materials. This property characterizes the internal reaction of the polymer to external air.action, expressed in deformation - a change in shape according topolymer sample. The deformation and strength properties of polymers depend on the size and flexibility of macromolecules, intermolecular interactions, temperature, physical and phase state of polymers, and other factors.

For a comparative assessment of the flexibility of macromolecules of various polymers, their chains are freely articulated, consisting of segments called statistical segments. Each of the segments includes as many monomeric units as necessary so that it can rotate freely relative to the previous segment.

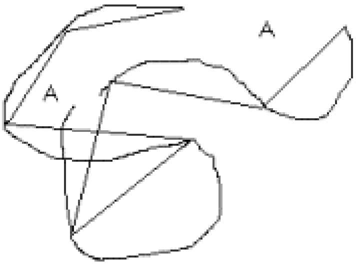


Fig.1. Polymer chain formed from random segments.

Thus, the statistical segment, or as it is also called the Kuhn segment (A), is a measure of freedom of rotation in real macromolecules and, accordingly, a measure of their flexibility. Table 2 of the appendix shows the A values of some polymers and the number of monomer units included in the segment.

Electrical Properties

The behavior of polymers in an electric field is characterized by electrical conductivity. Most polymers are dielectrics, i.e. characterized by high resistance and low conductivity when voltage is applied. For many polymeric materials, the phenomenon of static electrization is characteristic - the accumulation and conservation of an electric charge in the process of production, processing and operation.

Semiconductors are polymers that have an electrical conductivity of 10-3 - 10-9 S/m. These include polymers with conjugated double bonds, polymer complexes with charge transfer, as well as dielectrics filled with a conductive filler.

Waterproofing properties

A number of polymers have high hydro- and vapor barrier properties. Their water absorption ranges from tenths to hundredths of a percent. This allows them to be used in anti-corrosion technology.

Polymers have high adhesive, sealing, soundproofing and other useful technological properties, due to which they are widely used in construction.

Important properties of polymeric materials (PM) are high corrosion resistance and water resistance, which allows them to be widely used in anticorrosion technology. However, the myth about the "eternity" of polymers turned out to be somewhat exaggerated. PM are not universal in terms of resistance to any media. The degree of corrosion resistance of PM depends primarily on the properties of the polymer itself, as well as on the chemical composition and conditions of its exposure to an aggressive environment.

During corrosion of polymeric materials, the structure, molecular weight, chemical composition, as well as the interaction forces of individual macromolecules can change.

The impact of an aggressive environment on PM can manifest itself in a change in their structure and properties, or without violating the integrity of the material, i.e. without its destruction, or be accompanied by destruction.

Theoretical concepts of the corrosion of polymeric materials lag noticeably behind the theory of elastic, plastic, and highly plastic deformations, since corrosion is a non-equilibrium process and, in most cases, non-stationary.

In recent years, the attention of researchers to the problem of the durability of polymers has increased, and a number of interesting scientific and practical results have been obtained.

The corrosion of polymers is the result of overcoming the forces of interaction between atoms or molecules, which occurs under the influence of various oxidizing agents, thermal, radiation, mechanical interactions and other energy factors, as well as during chemical interaction with various aggressive media. As a result, various destructive processes occur in the polymer.

Under external influences of oxygen, heat, air moisture, light rays, the polymer is simultaneously exposed to several types of influences. In this regard, during polymer corrosion, various processes occur simultaneously. When analyzing the corrosion behavior of polymers, the dominant ones should be chosen.

Plasticization of polymers

plasticizingpolymers - the introduction of low-volatile low-molecular substances into them (**plasticizers**), increasing their plasticity and (or) elasticity.

Plasticizers reduce the brittleness, glass transition and fluidity temperatures, reduce the yield strength or forced high elasticity due to a decrease in the intensity of interaction between macromolecules and facilitate the mobility of their segments.

The effectiveness of a plasticizer depends on its compatibility with the polymer. The plasticizer separates ("sweats") above a certain limit, which determines the lower operating temperature of the plasticized polymer, since compatibility decreases with decreasing temperature.

Sometimes the plasticity of a polymer is increased by the addition of substances incompatible with it. It is assumed that such plasticizers weaken bonds not between individual macromolecules, but between elements of the supramolecular structure (structural plasticization).

Plasticization affects not only the mechanical, but also the dielectric properties and electrical conductivity of the polymer, which is taken into account when selecting plasticizers.

Plasticization is the introduction of substances (plasticizers) into polymers that increase the elasticity and / or plasticity of the material under the conditions of its operation and / or processing.

There are several methods of plasticization:

External (primary) plasticization - plasticization with substances that do not chemically bind to the polymer and can be removed by evaporation, extraction, etc.

Internal (secondary) plastification - plastification with substances that chemically bind to the polymer, as a result of which the properties of the plasticized materials are stable over time.

External plasticization, in turn, is divided into structural and molecular. A molecular plasticizer, a type I plasticizer, is thermodynamically compatible with the polymer and acts like a solvent. A structural plasticizer, a plasticizer of the second kind, is thermodynamically incompatible with a polymer and acts at the level of large supramolecular structures.

Thermodynamic aspect of plasticization

The "Polymer - Plasticizer" system is considered in thermodynamics as the "Polymer - Solvent" system, in which the plasticizer plays the role of a solvent, which is mainly distinguished by its lower volatility.

The compatibility of a polymer with a plasticizer depends on many factors, including the nature of the polymer and plasticizer, their ratio in the mixture, temperature, pressure, the presence of foreign substances, etc.

Compatibility can be most clearly judged by phase diagrams in the "Temperature - composition" coordinates. A typical view of diagrams is in the figure.

These are diagrams with the upper critical dissolution temperature (UCST). At temperatures $T>Tcr$ for any composition of the mixture, the polymer and plasticizer form a single-phase stable solution. At temperatures $T < Tcr$ in a certain range of compositions, the mixture decomposes into two phases, one of which is an almost pure plasticizer, the other is a concentrated solution of the polymer in the plasticizer.

Phase diagrams are of great practical importance, because allow at any temperature and any composition of the mixture to determine whether a stable system will form or phase separation will occur. Separation can manifest itself through the "sweating" of plasticizer drops on the surface of the polymer, clouding of the material. And if the plasticizer is crystallizing, then in its crystallization and destruction of the material.

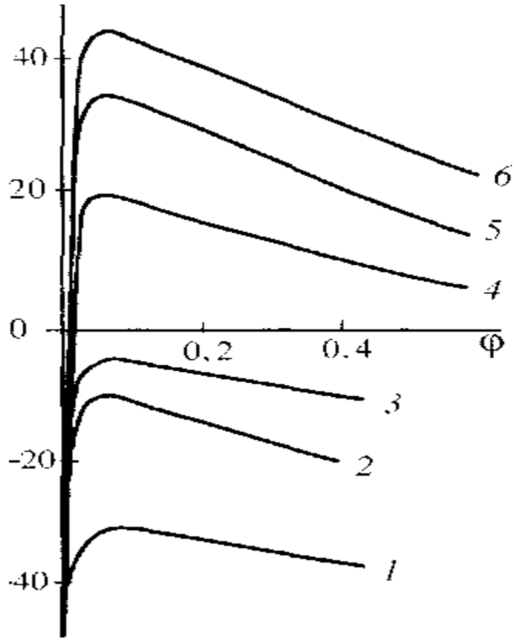


Figure 1. Phase diagrams of polystyrene - phthalates systems:
1 - dimethyl phthalate; 2 - diutilphthalate; 3-dihexyl phthalate; 4-dioctylphthalag;
5- dinonyl phthalate; 6-didecyl phthalate.

Mechanisms and effectiveness of the plasticizing action

In the event that the plasticizer is thermodynamically compatible with the polymer, the mechanism of the plasticizing action can be described as follows:

- plasticizer molecules, having a high affinity for the polymer, gradually penetrate into any structural formations, gradually destroying them and, being distributed among the polymer macromolecules, weaken the interaction of the latter with each other. If the polymer and plasticizer are non-polar, then this process has an entropic nature, i.e. the plasticizer acts as a simple thinner. If the polymer and the plasticizer are polar, then there is an interaction between the polar groups (solvation), as a result of which the interaction between the macromolecules decreases. In this case, this process is energetic in nature.

Due to the decrease in intermolecular interaction, the kinetic flexibility of polymer chains increases, and the free volume increases. As a result, the glass transition temperature of the polymer decreases, the regions of the highly elastic state expand, elasticity (ability to large reversible deformations) is retained at lower temperatures, and the strength of the material and the modulus of elasticity decrease.

The first theoretical consideration of the process of molecular plasticization was carried out by Zhurkov. He considered the process of plasticization of polymers having polar groups with polar plasticizers. It is known that polar polymers have sufficiently high glass transition temperatures precisely due to the implementation of a strong intermolecular interaction between polymer chains over polar groups, which leads to a strong limitation of chain mobility and an increase in their rigidity. As mentioned above, plasticizer molecules compatible with the polymer penetrate into the intermolecular space and solvate the polar groups of the polymer, thereby preventing their interaction with each other and increasing their mobility. Obviously, in this case, the more moles of the plasticizer will be introduced into the polymer, the less polar groups of the polymer will remain, capable of intermolecular interaction, the more the glass transition temperature will decrease. From here one can write:

$$\Delta Tc = k\, n,$$

where ΔTc · is the difference between Tc of the plasticized and non-plasticized polymer, which characterizes the efficiency of the plasticizing action, k· is the coefficient of proportionality, n is the number of moles of the plasticizer.

This equation is called Zhurkov's rule or the rule of molar concentrations. This rule is not always followed in practice, because the effectiveness of the plasticizing action also depends on the size and shape of the plasticizer molecules, especially when it comes to non-polar or low-polarity polymers and plasticizers.

For the plasticization of non-polar and low-polar polymers, Kargin and Malinsky proposed another expression:

$$\Delta Tc = k\, \varphi,$$

where k· is the coefficient of proportionality, φ is the volume fraction of the plasticizer.

This equation is called the rule of volumetric concentrations. This dependence is due to the fact that in the case of nonpolar polymers and plasticizers, the main role is played not by energy factors (interaction between polar groups), but by entropy factors: the greater the volume occupied by molecules of a low molecular weight substance in the "Polymer - Plasticizer" system, the greater the mobility of polymeric chains, the lower the glass transition temperature. The rule of volumetric concentrations is also not always fulfilled.

In the case when the plasticizer is thermodynamically incompatible with the polymer (a very narrow compatibility area is observed on the phase diagram or it does not exist at all at real temperatures), then plasticization is called structural and the mechanism of the plasticizing action is different. The plasticizer molecules, which have a low affinity for the polymer, do not penetrate into the intermolecular space, but enter only into the interstructural space. Moreover, these are not supramolecular structures that have a fluctuation character (associates), but macroscopic structural units, for example, separate crystalline regions. In this case, the plasticizer molecules are adsorbed on the interstructural interface, forming monomolecular layers that play the role of a kind of "lubricant" between the structural elements.

As a result, the mobility of these structural elements increases, the deformation properties of the material change: the strength and modulus of elasticity increase due to the orientation of supramolecular structures under the action of the load along the axis of the force.

The difference between these two mechanisms is clearly reflected in the dependence of the glass transition temperature of the plasticized polymer on the content of the plasticizer (Figure 2).

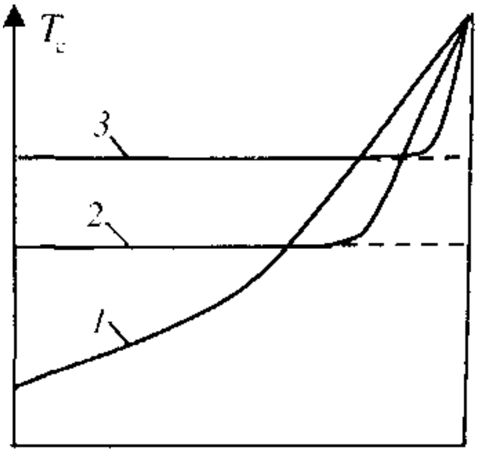


Figure 2 Change in Tc during molecular (1) and structural (2,3) plasticization

In the first case, the glass transition temperature decreases monotonically down to the glass transition temperature of the plasticizer itself. In the second case, a sharp drop in the glass transition temperature of the polymer occurs when fractions of a percent of a structural plasticizer are introduced into it, and then Tc stops changing, because an increase in the thickness of the lubricant layer does not affect the mobility of the structures.

Structural and molecular plasticizers are different substances. The structural ones include castor oil, chlorinated paraffin, etc. The molecular ones include phthalates, phosphates, sebacates, oligoethers, etc.

Factors affecting the effectiveness of the plasticizing action, and requirements for plasticizers

The main factors affecting the effectiveness of the plasticizing action are the chemical structure of the polymer and plasticizer, their thermodynamic compatibility, the volume and shape of the plasticizer molecules, their ability to undergo conformational transformations (their flexibility).

Thus, the influence of the nature of the polymer is manifested as follows: the more rigid the polymer chain, the greater the efficiency of the plasticizer (ΔTc). For polymers with high chain rigidity (for example, cellulose derivatives), the glass transition temperature of which lies in the region of very high temperatures and even above the thermal decomposition temperature, the introduction of 30-40% of the mass. plasticizer can lead to a decrease in Tc by 100 - 120 ºC. At the same time, for rubbers - flexible-chain polymers - whose Tg is already low (up to -70 ºC), the introduction of a plasticizer can only lead to a slight decrease in Tc by 10-20 ºC.

An analysis of the influence of this and other factors, as well as the features of the processing and operation of polymer plasticized materials, make it possible to formulate the main requirements for plasticizers:

- The plasticizer molecules must have optimal sizes, which ensure, on the one hand, their penetration into the intermolecular space of the polymer and a decrease in the glass transition temperature, and, on the other hand, a high boiling point and low volatility.
- The optimal shape of the plasticizer molecules is elongated.
- The plasticizer molecules must be capable of conformational transformations.
- The molecular plasticizer must be compatible with the polymer over a wide range of processing, storage, and operating temperatures.
- The plasticizer must have high frost resistance, i.e. do not crystallize in the temperature range of processing, storage and operation.
- The plasticizer should have as low a viscosity as possible, which will reduce the viscosity of the polymer material during its processing.
- Requirement of non-toxicity or low toxicity.
- The requirement of chemical compatibility with other components of the polymeric material (do not accelerate the decomposition of the components).
- Special requirements for plasticizers associated with the specifics of the use of a polymeric material can be very different, for example, when using a polymeric material in an aqueous medium, the plasticizer obviously should not dissolve in water; to nitroglycerin - a plasticizer of cellulose nitrate in the compositions of ballistic powders - not only requirements are imposed to reduce the Tc of the compositions, but also energy requirements.

Lecture 19
Theory of polymer solutions.

Plan:

1. History of the development of the theory of solutions.
2. True and real solutions.
3. Solubility of polymers and factors affecting it. 4. Thermodynamic evaluation of solubility.

True solutions of HWCs differ sharply in their properties from solutions of low molecular weight compounds:

1)The osmotic pressure of HWC solutions does not obey the van't Hoff law.

Usually, the experimentally determined value of the osmotic pressure of HMS solutions is much higher than the value calculated using the van't Hoff equation. This is explained by the fact that, due to its flexibility, the macromolecule behaves in solution like several shorter molecules. As the concentration increases, the number of segments of the macromolecule increases, which behave independently of each other. To calculate the osmotic pressure π of HMS solutions, the following equation is proposed:

$$\pi = \frac{CRT}{M} + BC^2,$$

where C is the mass concentration of the solution;

M is the molar mass of the polymer;

T is the absolute temperature;

where B is a constant depending on the nature of the solvent.

2) Diffusion rate of polymer macromoleculesis small, it is comparable with the diffusion rate of typical colloidal particles.

To calculate the diffusion coefficient of the HWC, the Einstein equation is applicable:

$$D = \frac{RT}{N_A} \cdot \frac{1}{B} = \frac{kT}{B};$$

where B is the coefficient of friction of diffusing particles of a given shape.

For spherical particles B = 6πηr. However, HWC macromolecules rarely have a shape close to spherical.

3) HWC solutions are able to scatter light, although to a lesser extent than typical colloidal systems. In HMS solutions, the Tyndall effect is not quite clearly detected due to the fact that the refractive index of solvated particles of the solute n differs little from the refractive index of the solvent n0, so the difference (n – n0) > 0, but the intensity of light scattering by HMS solutions is insignificant. For the same reason, macromolecules cannot be detected under an ultramicroscope. In addition, macromolecules are commensurate with colloidal particles only in length, and in other directions they correspond to the sizes of ordinary molecules.

4) HWC solutions are highly viscous. Only very dilute solutions obey the laws of Newton and Poiseuille (see "Viscosity of the Navy").

5)HWC solutions are true solutions, aggregatively stable systems. However, when**addingelectrolytes, the release of macromolecular compounds from the solution is observed**. This phenomenon is called salting out (see "Stability of HWC solutions").

6) HWC solutions are characterized by the phenomenon of coacervation. Coacervation is separationsystemsinto two phases, one of which is a solution of HMC in a solvent, and the other is a solution of a solvent in HMC, with a change in temperature or pH, or with the introduction of low molecular weight substances (see "Stability of HWC solutions").

7)For HMS solutions, the phenomenon of spontaneous, spontaneous changes in viscosity during long-term storage of solutions is characteristic. This phenomenon is called solution aging. Aging occurs either as a result of the degradation of polymer macromolecules or as a result of the binding of macromolecules. Aging occurs under the influence of oxygen and some other impurities.

8)With an increase in the concentration of HMW solutions, a change in temperature, or when an electrolyte is added, a spatial network may form, leading to the formation of jelly (see "Stability of HWC solutions").

The main factors that determine the structure and rheological properties of a dispersed system are the concentration of particles of the dispersed phase and the interaction energy of particles. In dilute aggregatively stable disperse systems, particles retain complete freedom of mutual movement, or, as they say, there is no definite structure. Such systems are Newtonian.

Their viscosity is described by Einstein's law: the viscosity of a dispersed system (sol, suspension) increases with an increase in the content of the dispersed phase.

This relationship is expressed by the equation:

$$(\eta - \eta0) / \eta0 = k\ \varphi,$$

where η and $\eta0$ are the viscosities of the colloidal solution and the dispersion medium, respectively;

$\varphi = Vd/V$ is the volume fraction of the dispersed phase (Vd) in the total volume of the system (V);

k is a constant depending on the particle shape.

The physical meaning of this law is that the relative increase in viscosity is directly proportional to the relative content of the dispersed phase in the system. The larger the volume fraction of the dispersed phase in the system, the more pronounced the inhibitory effect of the part on the fluid flow (straight line I in Fig. 5).

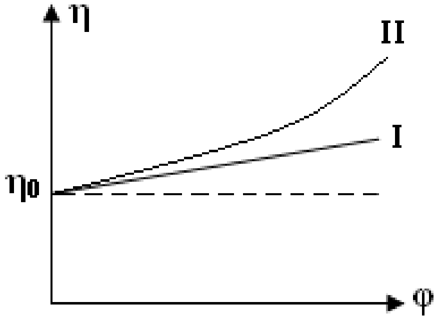


Fig.5 - Dependence of viscosity on the volume fraction of the dispersed phase for: I – structureless (Newtonian) disperse system; II - structured (non-Newtonian) disperse system.

Structured colloidal systems do not obey Einstein's law. For them, the value of viscosity increases with an increase in the content of the dispersed phase much more strongly than follows from the Einstein equation (curve II in Fig. 5).

According to modern concepts, sufficiently flexible HMS molecules in solution are in the form of random coils impregnated with a solvent. The presence of such coils, as well as the formation of structures in solution, causes an anomalous dependence of the viscosity of polymer solutions on their concentration, which does not obey the Einstein equation. HWC solutions are non-Newtonian liquids.

The concentration dependence of the specific viscosity of not too concentrated polymer solutions is usually satisfactorily described by the equation proposed by Huggins:

$$\frac{\eta_{уд}}{C} = [\eta] + k1[\eta]2C,$$

$\eta sp = (\eta - \eta0) / \eta0$ - specific viscosity (see Table 1);

where $[\eta]$ is the intrinsic viscosity (see Table 1);

C is the concentration of the solution, g/100 ml;

k1 is a coefficient called the Huggins constant.

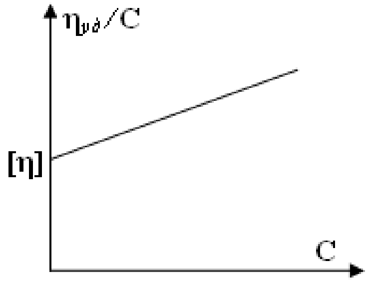
The coefficient k1 characterizes the interaction of macromolecules in the polymer–solvent system. Its value is practically independent of the molar mass of the polymer and varies only depending on the nature of the solvent. In solvents interacting with HMS, the value of the Huggins constant is 0.2 - 0.3.

Table 1

Designations and names of quantities adopted in viscometry of polymer solutions

Value designation	**Name**
ηrel = η/η0	Relative viscosity
ηsp = (η − η0)/η0 = ηrel − 1	Specific viscosity
ηpr = ηsp/C	Reduced viscosity
ln ηrel /C	Logarithmic reduced viscosity
[η] = (ηsp/C)C→0 == (ln ηrel /C) C→0	Intrinsic viscosity

Intrinsic viscosity, which reflects the hydrodynamic resistance of polymer molecules to fluid flow, can be determined for dilute polymer solutions in which the interaction of macromolecules can be neglected. To find the intrinsic viscosity, the dependence of the reduced viscosity on the concentration is established in a narrow range of low concentrations, and the results obtained are extrapolated to zero concentration (Fig. 6).



Rice. 6 - Graph for determining the intrinsic viscosity of the HWC solution

The relationship between the intrinsic viscosity of the HMS solution and the molar mass of the polymer is satisfactorily described by the empirical Mark-Houwink equation:

[η] = K Mα,

where α is a constant (like "K") for a given polymer homology series in a particular solvent at a particular temperature. The constant "α" reflects the degree of coagulation of the polymer molecules and the flexibility of the chain. For rigid rod-shaped molecules α ≈ 1, for flexible molecules folded into a globule α ≈ 0.5.

Knowing the intrinsic viscosity of the HMS solution, the Mark-Houwink equation can be used to determine the molar mass of the polymer:

$$M\alpha = [\eta]/ K \text{ or } \lg M = \frac{\lg([\eta]/K)}{\alpha}.$$

It should be noted that the obtained value of the molar mass is average, since any real polymer is a polydisperse mixture of macromolecules.

Lecture 20
The process of dissolving polymers.
Plan:

1. Phase diagrams for polymer-solvent systems.
2. Swelling of polymers.
3. Swelling kineticsI.
4. Association andsolvationpolymer solutions.

The only factor that distinguishes the thermodynamics of mixing polymers from the thermodynamics of mixing low molecular weight liquids is the large molecular weight of the components. Consider the thermodynamics of mixing two high-molecular liquids.

When mixed, polymers can form a true solution. The condition for the formation of such a solution is the fulfillment of the well-known inequality:

$$\Delta Gcm = \Delta H - T\Delta S < 0$$

where ΔGcm is the Gibbs free energy of mixing, ΔH is the heat of mixing, ΔS is the entropy of mixing, T is temperature.

If this condition is met, then when two polymers are mixed, a homogeneous single-phase system is formed. At $\Delta Gcm > 0$, the polymer mixture is a two-phase colloidal system.

The properties of polymer mixtures fundamentally depend on the phase state of the mixture. It is clear that if we want to predict the properties of mixtures, then it is very important to know what determines the mutual solubility of polymers. It is determined by the signs and values of ΔH and ΔS. When mixing liquids, the entropy in the vast majority of cases increases, which contributes to their solubility. For ideal gases, the entropy of mixing is determined by the number of possible permutations (combinations) of molecules and, according to Gibbs, is equal to:

$$\Delta S = -R(N1 \bullet \ln N1 + N2 \bullet \ln N2)$$

where N is the number of mixed molecules of each component, R is the gas constant.

The polymer molecules are large, but their number is small, as is the number of possible permutations in the mixture. Therefore, the combinatorial entropy of mixing of two polymers is small. The larger the molecular weight of the polymers, the smaller the entropy increment upon mixing, and for a pair of very high molecular weight polymers, the ΔS of mixing is close to zero. Therefore, the mutual solubility of polymers is determined mainly by the enthalpy (heat) of mixing, which depends on the energy of intermolecular interaction.

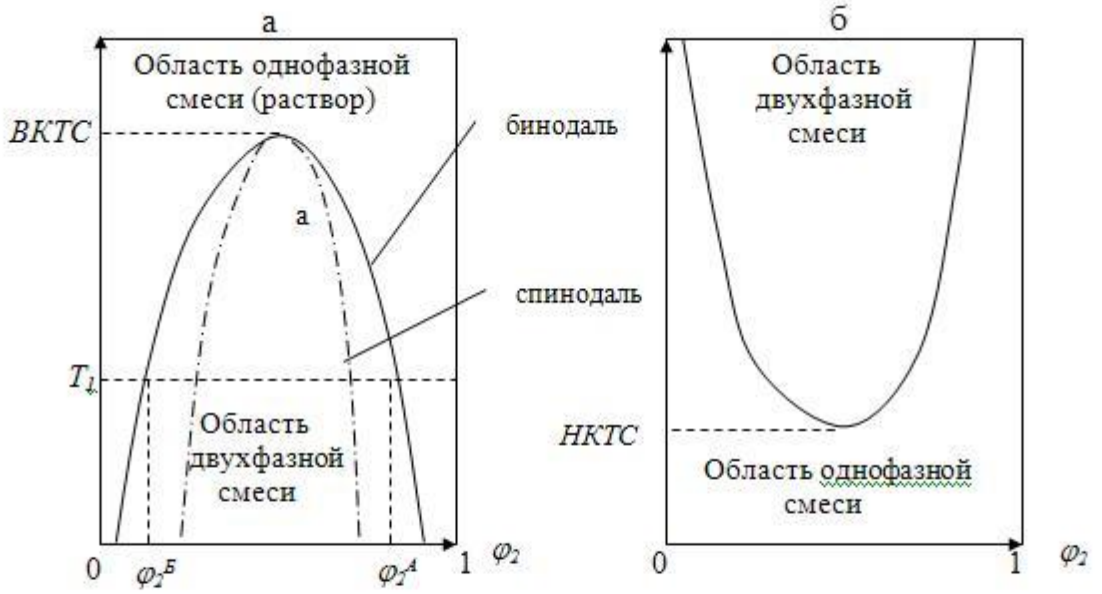
To form a solution with a mixture of polymers, the value of $T\Delta S$ must be greater than ΔH. Therefore, even at the minimum positive value of ΔH, the mixture of polymers will be heterogeneous. For the dissolution of polymers, it is necessary that the value of ΔH be negative or equal to zero. To do this, heterogeneous macromolecules of the mixture must have a higher intermolecular interaction energy than homogeneous ones ($\Delta H < 0$); or the interaction energies of homogeneous and heterogeneous macromolecules must be equal ($\Delta H < 0$). For nonionic substances, which are the majority of hydrocarbon polymers, the probability of the above condition is rather small (for example, the solubility of polymers in low molecular weight liquids is due in most cases to an increase in the entropy of the system upon mixing). Mutual solubility should be expected only for a pair of polymers with a very similar chemical structure ($\Delta H < 0$), or for polymers containing chemical groups capable of strong physical interaction ($\Delta H < 0$). Pairs consisting of polar and non-polar polymers have very low mutual solubility, not exceeding a fraction of a percent.

All real polymer-polymer systems are mutually soluble within certain limits. The phase diagram provides the most complete description of the magnitude of the mutual solubility of polymers at different temperatures.

The curve that separates the region of a two-phase mixture from the region of metastable states in the phase diagram and is called the spinodal is determined by the expression: **ΔGcm/2=0**

The curve separating the region of metastable states from the true solution is called the binodal and corresponds to the equality:

As experimental studies have shown, there are very few completely mutually soluble polymer pairs. The mutual solubility of the vast majority of polymer pairs in a wide temperature range is a percentage or a fraction of a percent. A very small difference in the polarities of the two polymers leads to the fact that their mutual solubility is tenths or even hundredths of a percent. Even such chemically similar polymers as polyethylene and polypropylene or polybutadiene and polyisoprene, or polymethyl methacrylate and polybutyl methacrylate have a mutual solubility of several percent.



Rice. Fig. 5. Phase diagram of a mixture of two polymers with (a) the upper *critical mixing temperature UCTS and (b) the lower critical mixing temperature LCST.*

There are few polymer pairs with high mutual solubility (20% or more). These are mainly oligomers or copolymers, differing only in the ratio of monomer units in the chain. Other rare examples of soluble pairs are, for example, polystyrene and polyvinyl methyl ether, polymethyl methacrylate and vinylidene fluoride, polyvinyl chloride and poly-α-caprolactone. In most cases, their solubility is due to a rather high polar interaction between dissimilar macromolecules, which leads to a negative mixing ΔH.

Thus, the vast majority of pairs of amorphous polymers upon mixing form two-phase mixtures. Among crystalline polymers, the pairs that form common crystallites are still unknown. Such a "general incompatibility" of polymers caused for some time a negative attitude of many scientists towards the prospects of mixing polymers. But with great advances in polymer blends, that attitude has changed.

In true solutions separated from the solvent by a semipermeable partition, osmotic pressure can be measured, the value of which depends on the concentration of the dissolved substance and for dilute solutions is described by the van't Hoff equation, where C is the mass concentration, kg/m3.

Graham tried to determine the osmotic pressure of colloidal solutions and came to the erroneous conclusion that colloidal systems do not have this property. As you know, it was on this erroneous fact that Graham made the division into true solutions and colloidal systems. However, the fact that particles in a colloidal state also perform chaotic motion leaves no doubt that colloidal systems must also have osmotic pressure.

The number of particles in a colloidal system is very small compared to a true solution, so the osmotic pressure of the sols is also very low. For example, a 1% gold sol with particles r» 10-9m has an osmotic pressure p = 3.45 Pa. In order for this sol to have the same osmotic pressure as a 1 M electrolyte solution, it would be necessary to disperse 50 kg of gold with particles r = 10-9 m in 1 dm3.

Obviously, at a low osmotic pressure of a sol, even the slightest electrolyte impurity will have a tremendous effect on the osmotic pressure; therefore, when studying osmosis in sols, they must be thoroughly purified. Smoluchowski showed that with a change in the degree of dispersity of the colloid, the osmotic pressure is inversely proportional to r3 particles, i.e. p1/p2 = (r2/r1)3.

The osmotic pressure of a solution of a high molecular weight substance also differs from the osmotic pressure of a solution of a low molecular weight substance. In the region of dilute solutions, the osmotic pressure of dissolved polymers will be greater than that of sols. The molecular weight of macromolecular compounds can be determined by measuring the osmotic pressure. According to the slope of the dependence described above, the intensity of the interaction of macromolecules with the solvent, characterized by the value of A2, is determined. At the same mass concentration in polymer solutions, large molecules are present in a smaller amount than the number of molecules of low molecular weight substances, so the osmotic pressure in such solutions will be lower than in solutions of low molecular weight substances.

Osmotic pressure - solution - polymer

Osmotic pressure of polymer solutions determined in an instrument called an osmometer. This is a device in which the osmotic cell with the solution is separated by a semi-permeable partition from the pure solvent and connected to a narrow capillary. As the solvent penetrates into the cell, the solution rises through the capillary until the osmotic pressure is balanced by the weight of the hydrostatic column in the capillary. The greater the concentration of the solution, the more the solvent penetrates, the greater the osmotic pressure. However, with an increase in the polymer concentration, the viscosity of the solution increases significantly, which makes it difficult for the solution to rise along the osmometer capillary. There are only a very small number of works in which the osmotic pressure of solutions was determined in the region of higher concentrations.

Osmotic pressure of polymer solutions, having a high molecular weight, corresponds to a solvent column no more than a few centimeters high, therefore, given the need for extrapolation to infinite dilution, special measures must be taken to ensure high measurement accuracy.

Measuring the osmotic pressure of a polymer solution of a certain concentration with a known MB (reference solution) is the most reliable way to test an osmometer. As a reference, either a monodisperse polymer, such as polystyrene or poly-a-methylstyrene, obtained by anionic polymerization according to the Schwartz method, is used. The absence of low molecular weight fractions in these reference samples guarantees reliable and reproducible results. The osmotic pressure of reference sample solutions must be reliably established in preliminary experiments with validated osmometers.

How is the osmotic pressure of a polymer solution related to its concentration and molecular weight.

The method of measuring the osmotic pressure of polymer solutions makes it possible to calculate the molecular weight of the polymer.

Direct measurements of the osmotic pressure of polymer solutions can be carried out using semipermeable membranes that freely pass solvent molecules and are impermeable to polymer macromolecules. Such membranes are usually made from slightly swelling but insoluble polymer films, most often cellulose films. In the manufacture of membranes under laboratory conditions, the film is usually cast from cellulose ether, and then the ether is saponified.

The determination of the osmotic pressure of polymer solutions was carried out at a temperature of 27 0, and the following, essentially static method of measurement was used: after washing the osmometer, determining the zero point and filling the right half of the cell with the test solution, the device was left for 2–3 hours for a uniform distribution of low molecular weight impurities over both side of the membrane. Then the expected value of the difference in levels in the capillaries was established and every 30 min.

Direct measurements of the osmotic pressure of polymer solutions can be carried out using semipermeable membranes that freely pass solvent molecules and are impermeable to polymer macromolecules. Such membranes are usually made from slightly swelling but insoluble polymer films, most often cellulose films. In the manufacture of membranes under laboratory conditions, the film is usually cast from cellulose ether, and then the ether is saponified.

In addition, with increasing concentration, the osmotic pressure of polymer solutions does not increase linearly, while according to the van't Hoff law

Lecture 21.

Hydrodynamic properties of polymer solutions.

Plan:

1. Hydrodynamic properties of polymer solutions.
2. Relative, reduced and intrinsic viscosity.
3. Relationship between molecular weight and intrinsic viscosity.

Specific properties of polymersare mainly due to two features: 1) the existence of two types of bonds - chemical and intermolecular, holding macromolecular chains around each other; 2) the flexibility of the chains associated with the internal rotation of the links. As a result, the macromolecule can change its spatial form by changing from one conformation to another. As a result of conformational changes, macromolecules can either coagulate, forming globules and coils, or straighten and fit into oriented structures - bundles. The most probable conformation of the HMC molecule is a coil, or globule. The flexibility of polymer chains depends on the chemical structure of the chain, the nature of substituents, their number and distribution along the length of the chain, and the number of links in the chain.

Solutions of HMC, as well as solutions of low molecular weight compounds (LMC), are homogeneous, thermodynamically equilibrium and aggregatively stable systems. These are true solutions.

However, the properties of HMS solutions (Table 1) differ significantly from those of NMS solutions. The difference lies in the fact that HMS solutions have a low diffusion rate, low osmotic pressure, and a significant viscosity than the NMS solutions corresponding to them in concentration. HWC solutions also have properties. Not inherent in NMS solutions: light scattering, thixotropy.

Thixotropy– the ability under isothermal conditions to spontaneously restore its structure after mechanical destruction.

Table 1

Characteristics and properties of various disperse systems

Characteristics and properties	**Solutions true**	
	Low molecular weight substances	**Navy**
1. Dispersological characteristic	***homogeneous system***	

1.1. Dispersion medium	liquid	Liquid
1.2. Dispersed phase	Molecules, ions	macromolecules
1.3. Interface	No	No
1.4. Particle size of the dispersed phase, nm	Up to 1 (up to 10-9 M)	1-100 (10-9 - 10-7 m)
2. Sustainability		
2.1. Aggregative	Resistant	Resistant
2.2. thermodynamic	Resistant	Resistant
3. Physical properties		
3.1. Diffusion	well expressed	Weakly expressed
3.2. Dialysis	going on	Not happening
3.3. Osmotic pressure	high	Low
3.4. Brownian motion	Eat	Eat
3.5. Tyndall cone	No	No
3.6. Viscosity	Low	Relatively high
3.7. Ultrafiltration capability (filter pore diameter less than 1 nm)	Eat	No
3.8. Possibility of filtering through a paper filter	Eat	Available for non-viscous solutions
3.9. Possible phenomena under the influence of electrolytes, alcohol, syrups, glycerin	Change in solubility	Salting out (dehydration)

The dissolution of the occurs spontaneously, but has a characteristic feature, the dissolution is preceded by swelling, which consists in an increase in the volume and mass of the polymer due to the absorption of a certain amount of solvent by it. The quantitative measure of swelling is the degree of swelling α, which can have a volume or mass expression:

$$\alpha = \frac{m - m_o}{m_o} \quad \text{yoki} \quad \frac{V - V_o}{m_o}$$ α = or where α is the degree of swelling;

V0 and V, m0 and m are the volumes and masses of the initial and swollen polymer, respectively.

The reason for the swelling is the difference in the properties of the two components - HWC and NMS. The rate of this process is determined by the mobility of molecules, their diffusion coefficient. The specificity of the swelling of polymers lies in the fact that molecules interact and mix, which differ from each other by many orders of magnitude in their size and mobility. Therefore, the transition of macromolecules to the solvent phase occurs very slowly, while NMS molecules quickly penetrate into the polymer network, pushing the chains apart and increasing its volume.

The flexibility of the chains facilitates the penetration of small molecules into the polymer network. That is, the swelling process is a one-way displacement due to a large difference in the size of the molecules.

The ability to swell is a property of the polymer, determined by its composition and structure, as well as its structural and mechanical properties. Therefore, the swelling process is always specific. The polymer swells not in any, but only in the "good" solvent with which it interacts. This interaction is related to polarity. Therefore, polar polymers swell in polar liquids, for example, proteins in water, while non-polar polymers swell in non-polar ones (rubber in benzene).

Swelling may be limited or unlimited. In the first case, α reaches a constant limit value (for example, swelling of gelatin in water at room temperature), in the second, the values of m and α pass through a maximum, after which the polymer gradually dissolves (for example, gelatin in hot water). In this case, swelling is the initial stage of dissolution.

The swelling process can be divided into 2 stages. At the first stage, heat release ΔH occurs, contraction of the system is observed (a decrease in the total volume). The second stage is almost not accompanied by contraction and heat release, but is characterized by an increase in α and the volume of the swelling polymer.

Limited swelling usually ends in the second stage, unlimited swelling leads to the dissolution of the polymer. A partially swollen polymer is called jelly.

One of the factors affecting the process of swelling and dissolution of polymers is the degree of polarity of polymer units and solvent molecules. If the polarities of the chain links and solvent molecules are close to each other, then the swelling and dissolution of such polymers occurs relatively easily.

The second factor contributing to these processes is the flexibility of the polymer chains, since the dissolution process is associated with the separation of the chains from each other and their diffusion in the solvent.

The molar mass of the polymer is of certain importance in the processes of swelling and dissolution of HWCs, since with the elongation of the chains the interaction energy between them increases and more energy is required to separate them from each other. The higher the molar mass of the polymer, the more difficult it is to dissolve. The swelling process is also affected by temperature, pH of the medium, and the presence of electrolytes.

Lecture 22

Methods for determining the molecular weight of polymers.

Plan:

Most often, the number average molecular weight of polymers is found by the osmotic pressure method, which is based on studying the phenomenon of osmosis - one-sided penetration of solvent molecules through a semipermeable membrane that does not allow polymer molecules to pass through. The quantitative characteristic of the phenomenon of osmosis is the osmotic pressure, which is proportional to the number of molecules per unit volume of the solution.

Molecular weight is defined as a coefficient relating weight and partial concentrations

where C is the weight concentration, g/cm3; - total partial concentration, molecules/cm3; - molar concentration, mol/cm3.

Thus, the problem is reduced to determining the molar concentration of a solution of a known weight concentration.

The desire of solvent molecules to spontaneously penetrate the membrane is determined by the difference in the chemical potentials of the solvent in the parts of the system separated by a partition, and, since it is known from chemical thermodynamics that for solutions

where is the chemical potential of the solution at the activity of the solution a and the standard chemical potential.

Osmotic pressure of the solution $\pi = -\Delta\mu_1/\overline{V}_1$

where is the partial molar volume of the solvent, p - serves as a quantitative measure of the affinity between the components of the solution.

The relationship between osmotic pressure and the weight concentration of solutions is described by the following equations:

(van't Hoff equation) for solutions of low molecular weight substances

$$\pi = c_2/MRT$$

for polymer solutions

$$\pi = RT\left(\frac{1}{M}c_2 + A_2c_2^2 + A_3c_2^2 + \right)$$

or

$$\frac{\pi}{c_2} = \frac{RT}{M} + A_2RTc_2 + \cdots$$

where A2 is the second virial coefficient characterizing the interaction of the polymer with the solvent and the shape of macromolecules in solution, usually A3O.

Light scattering method. Weight average molecular weight

The phenomenon of light scattering in polymer solutions is observed if the size of macromolecules is less than l / 2 - half the wavelength of transmitted light. There are various theories of light scattering that underlie the calculation equations of experimental methods for determining the molecular weight. Provided that the size of polymer molecules is less than l/2, Einstein's theory of light scattering is valid for polymer solutions.

If light is scattered by spherical particles, then the scattering intensity will be the same in all directions. Let us denote the angle at which the intensity of the scattered light is determined with respect to the incident beam, Q. The scattering power is characterized by the scattering coefficient R:

$$R_{\Theta} = \frac{I_{\Theta}}{I_0}\frac{l^2}{v},$$

where IQ, I0 are the intensity of the scattered and incident light; l is the distance at which scattered light is observed from the scattering volume; v is the scattering volume.

In the practice of determining the intensity of scattered light, R90 is most often determined, i.e. scattering of light at an angle of 90o, although with the help of modern instruments, especially those using a laser as a light source, it is possible to determine the intensity of scattered light from Q = 4o.

The Debye equation is used to calculate the molecular weight of polymers:

$$\frac{Kc}{R_{\Theta}} = \frac{1}{\overline{M}_w} + 2A_2c ,$$

where c is the weight concentration, g/cm3; K is the optical constant depending on the refractive index of the medium (n0), the concentration increment of the refractive index of the solution (dn/dc) and the light wavelength l,

$$K = \frac{2\pi^2 n_0^2 (\mathrm{d}n / \mathrm{d}c)^2}{N_A \lambda^4}$$

Thus, to determine the molecular weight, one should measure the angular scattering of light, the refractive index of the medium. Particular attention should be paid to (dn/dc), since this value is usually extremely small. Instruments should be involved that make it possible to determine the refractive index with an accuracy of up to the 6th decimal place.

By analogy with the absorption of light, we can write for the scattering intensity

$$I = I_0 e^{-\tau v},$$

where τ is turbidity at v =1; I is the intensity of the light that passed through the solution after scattering.

Turbidity is related to the scattering coefficient by the relation

$$\tau = \frac{16\pi}{3} R_\theta .$$

Therefore, taking into account the equation, it is possible to calculate the molecular weight according to the equation

$$\frac{Hc}{\tau} = \frac{1}{M_w} + 2A_2 c ,$$

where H is the optical constant, H = 16p K/3.

To calculate the molecular weight, the value is determined

$$\lim_{c \to 0} \frac{Hc}{\tau} = \frac{1}{M_w} .$$

The angle of inclination can be used to determine the value of A2 and characterize the interaction of the components of the solution. Changes in temperature, replacement of the solvent can cause a change in the intermolecular interaction of the components of the solution and the shape of the macromolecules in the solution.

Molecules of solution and forms of macromolecules in solution.

Molecules can also acquire an asymmetric shape. In this case, the scattering of light at different angles to the incident beam will be uneven, and the found value of the molecular weight contains an error. Therefore, it is necessary to introduce a correction for the internal interference of light, which appears as a result of light scattering with a certain phase difference from different parts of the molecules. There are two main methods for introducing corrections: the Debye method and the Zimm method.

The Debye method is based on measuring the scattered light intensity at scattering angles of 135 and 45o, respectively R45 and R135. The intensity ratio is equal to the ratio of corrections P and is called the asymmetry coefficient

$$\mathbf{z = R_{45} / R_{135} = P_{45} / P_{135} .}$$

The value of z depends on the concentration of the solution, since the shape of the macromolecules in the solution can change with increasing concentration. To determine the true value of z, the dependence 1/(z-1)=fc is built and 1/([z]-1) = limc®0 1/(z-1) is determined.

Lecture 23
Polymer gel

Plan:

1. Concentrated polymer solutions.
2. Viscosity of concentrated solutions and hysteresis.
3. Jelly formation and jellies.

In colloidal solutions, suspensions and solutions of macromolecular compounds spontaneously or as a result of external influences, certain structures are formed that give disperse systems peculiar physical and mechanical properties: strength, elasticity (elasticity), plasticity, viscosity. These properties are called structural-mechanical, or rheological. The study of the structural-mechanical properties of disperse systems is of great importance for biology, medicine, soil science, and a wide variety of areas of modern technology.

In lyophobic systems, the adhesion of particles caused by the addition of an electrolyte or an increase in the concentration of the sol occurs most easily on the protruding areas of the surface of the particles - at the corners and ribs. Such a process begins in individual sections, and then spreads to the entire volume of the given system. In this case, all solid particles of the dispersed phase are bound into one continuous frame with a known strength. The gaps between the particles in the cage cells are filled with a dispersion medium, some of whose molecules are bound to the surface of the particles by the forces of intermolecular interaction, while the bulk of the liquid is held mechanically in the cells. The resulting system, approaching in its properties to a solid body, is called a gel.

The formation of a structure covering the entire volume of the system is possible only at a certain concentration of particles sufficient to build an integral framework. So, at room temperature, Fe (OH) 3 turns into a gel when a certain amount of electrolyte is added to it, if the Fe2O3 content in the solution is at least 1%, and the vanadium pentoxide sol turns into a gel when it contains 0.05% V2O5.

The minimum sol concentration at which the formation of a skeleton is possible depends significantly on the degree of dispersion of the system and on the shape of the particles. The smallest amount of substance needed to build a framework in a given volume is required when the particles are in the form of thin sticks or filaments with minimal dimensions. With a sheet-like shape of the particles of a substance, the formation of a skeleton will require a little more and even more - with an isodiametric shape of the particles (ball or cube).

In solutions of macromolecular compounds with linear macromolecules, the length of which far exceeds their dimensions in the other two directions, the conditions for the formation of the structure are even more favorable. The inhomogeneity of the surface of particles in such systems is determined by their chemical composition and structure. In solutions of high polymers, even with a relatively low concentration, especially with decreasing temperature, when the intensity of the thermal motion of molecules weakens, the attractive forces between molecules turn out to be greater than the repulsive forces, and the particles adhere to each other, forming a loose framework. At a sufficient concentration of the dissolved substance, structure formation extends to the entire volume, as a result of which the solution loses fluidity, while maintaining uniformity.

The transition of the HWC solution into jelly is facilitated by a number of factors: an increase in the concentration of the solution, a decrease in temperature, and the addition of substances to the solution that reduce the hydration of particles and, as a result, reduce the stability of the system. So, when electrolytes are added to a solution of a high polymer, the process of transition of the solution into jelly is mainly influenced by anions. All anions, according to their ability to influence the rate of gelation, can be placed in a lyotropic series of the same type that was considered in the study of the salting-out effect of anions. The more an ion exhibits the ability to hydrate, the more actively dehydration of particles occurs in its presence, which facilitates their connection with each other and the formation of a structure. The following is a list of anions according to their effect on gelling rate:

SO42->C4H4O6->CH3COO->CI->NO3->Br->I->CNS-

The ions at the beginning of the row accelerate gelation, and the ions at the end of the row slow it down.

Depending on the nature of the forces acting between the particles involved in the formation of structured systems, the structures that arise in various disperse systems are divided into two types by P.A. Rebinder:

1) Coagulation-thixotropic structures,
2) Condensation-crystallization structures.

The difference between the structures is determined by the nature and intensity of the interaction between the particles that form the system.

In coagulation-thixotropic structures, the particles approach each other and adhere under the action of forces of molecular attraction. Weak molecular bonds between particles can be broken by mechanical action on the structured system (stirring, shaking, etc.)

Breaking the bonds leads to the destruction of the structure: the particles that have lost the connection acquire the ability for random thermal motion. It is also important to note that in colloid-thixotropic systems, after the cessation of mechanical action on them, the destroyed structure spontaneously recovers after some time, while both destruction and restoration of the structure occur at a constant temperature.

Thus, structures resulting from the action of weak forces of molecular attraction between particles separated by thin liquid films are reversible structures. The reversible isothermal transformation of a structured system into a structureless system is called thixotropy.

As applied to colloidal systems, the phenomenon of thixotropy can be considered as an isothermal transformation of a gel into a sol according to the following scheme: gel - sol

This transformation is caused by the same factors that cause coagulation.

One of the characteristic mechanical properties of coagulation thixotropic structures is their plasticity. Plastic bodies under the influence of external forces irreversibly change their size and shape, which, after the termination of the action of external forces, are not spontaneously restored. At low strain rates, plastic bodies flow without noticeable destruction of the structure. The bonds broken in the process of deformation are restored at new points. At high strain (shear) rates, the bonds do not have time to recover, which entails a sharp destruction of the structural framework.

Condensation-crystallization structures are not plastic.

A characteristic feature of such structures is elasticity. Deformations caused in elastic bodies by external forces are reversible; upon termination of deformation, the body restores its shape and dimensions. If the forces applied to the elastic body exceed its tensile strength, brittle fracture of the structural frame occurs. Elasticity is possessed by jellies of protein substances, rubber starch, etc.

Many structured systems of both the coagulation type (gels) and the crystallization type (jelly) are characterized by the phenomenon of spontaneous compression of the structural framework, accompanied by the release of some part of the liquid from the structure. This process, which is a special case of the aging of colloidal systems, is called syneresis. Syneresis is quite common. Let's consider two examples. The staling of bread is the result of the separation of water from the jelly, which is bread, while the structure of the jelly becomes more durable and rigid. Starch paste and jelly release water when standing. The adhesive properties deteriorate.

It is often convenient to study the processes of structuring and destructuring in dispersed systems by observing the change in them of a property typical of liquid systems - viscosity, which is closely related to other rheological properties of systems. In this case, it should be taken into account that the viscosity of some lyophobic sols and especially solutions of macromolecular substances exhibits a number of anomalies:

a) not obeying the law of Newton and Poiseuille,
b) change over time,
c) abnormal behavior with temperature change,
d) change from mechanical influences (the phenomenon of thixotropy).

In such systems, additional viscosity appears due to additional resistance (friction) to the flow of liquid due to the formation of grid-like structures. This viscosity is called structural. Thus, the viscosity of these systems can be considered as the sum of two terms: normal viscosity, due to the normal, obeying the Newton and Poiseuille laws, laminar flow of the liquid, and structural viscosity.

The last term increases very rapidly with slight increases in the concentration of polymer solutions.

Gels differ both from dilute solutions, in which each colloidal particle or macromolecule is kinetically individual particles, and from compact coagulates or solid polymers. In a number of properties, gels occupy an intermediate position between solutions and solid polymers. Gels include various porous and ion-exchange adsorbents, ultrafilters and artificial membranes, muscle tissue fibers, cell membranes, cartilage, various membranes in the body.

Elastic gels, or jellies, formed by chain macromolecules of gelatin, agar-agar, rubber and other polymers differ in properties in many respects from brittle gels. Due to the flexibility of chains in a spatial network, elastic gels can relatively easily change their volume when absorbing or releasing a solvent, and retain their elasticity when dried. Elastic gels absorb only those liquids that can be solvents in relation to them.

The absorption of liquid by elastic gels is accompanied by a significant increase in the volume of the jelly or its swelling. The volume of the jelly can be ten times greater than the intrinsic volume of the polymer. The swelling may progress to complete dissolution of the polymer.

Some features of diffusion and reactions in jellies are of interest. In water jellies, in which the water content sometimes reaches 99% of their mass, diffusion occurs at almost the same rate as in pure water. The diffusion rate depends on the size of the diffusing particles; ions and small molecules diffuse faster than large colloidal particles.

Diffusion in jelly differs from diffusion in liquids in that there is no mixing and the formation of convection currents, which almost always occur in liquid solutions, is impossible.

In jellies, as well as in solutions, various reactions can occur. The absence of mixing and convection currents gives the reactions in the jelly a somewhat peculiar character: in different parts of the jelly, the reactions can proceed independently of one another. So, if one of the products of the reaction occurring in the jelly is a solid insoluble substance, then the phenomenon of periodic precipitation (Liesegang rings) is observed in the jelly instead of the formation of a precipitate throughout the volume. These periodic phenomena (reactions) can be observed in the reaction of silver nitrate with potassium bichromate. If you dissolve K2Cr2O7 in gelatin and then transfer the solution to jelly, then after applying a drop of AgNO3 solution around the drop, as a result of the reaction, a red-colored Ag2Cr2O7 precipitate is formed in layers (rings).

Such structures probably arise as a result of rhythmic reactions in the jelly.

Lecture 24
Polyelectrolytes
Plan:

1. Features of polyelectrolyte solutions.
2. Polyampholytes. isoelectric point.
3. Proteins - as representatives of amphoteric polyelectrolytes.
4. Ionic equilibrium of polyelectrolytes.
5. Interpolymer complexes. Practical significance of polyelectrolytes.

Polyelectrolytes are understood as those HWCs, the elementary link of which contains an ionogenic group (nucleic acids, proteins, polysaccharides, proteoglycans). They differ from non-electrolyte polymers (polyethylene, polystyrene, rubbers, polyvinyl chloride ...) in the same way as low molecular weight electrolytes from non-electrolytes. They are soluble in polymeric solvents and water, electrically conductive, and their properties are strongly affected by the Coulomb interaction of charges.

By the nature of the dissociation of ionogenic groups, polyelectrolytes are divided into:

1) polyelectrolytes containing only acidic groups in their composition, dissociating with the elimination of the H + ion (-COOH, -SO3H, -SH). Natural polymers include agar-agar, oxidized starch, and pectin. The composition of agar macromolecules includes sulfo groups, and the elementary units of oxidized starch and pectin contain carboxyl groups. In some polymers, the H+ ion in these groups may be replaced by a metal cation;

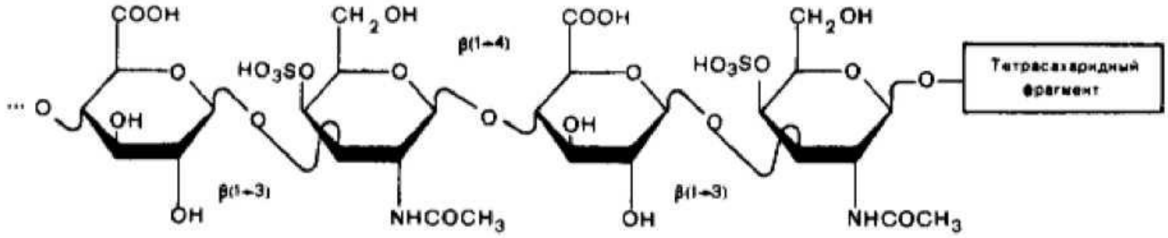
2) polyelectrolytes, the macromolecules of which contain only basic groups (for example, -NH2). There are no such compounds among biopolymers, they are obtained synthetically (anion-exchange resins - anion exchangers of great

practical importance);

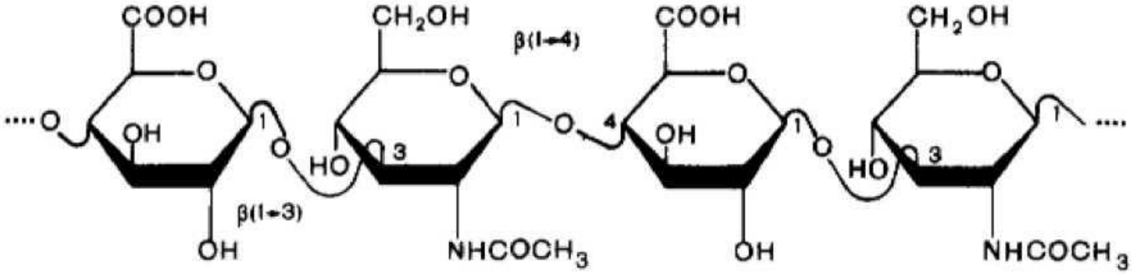
3) polyelectrolytes, in the macromolecules of which acidic and basic groups alternate, are polyampholytes. First of all, they are proteins.

Let's consider the structure of some of the most biologically important polyelectrolytes. Nucleic acids - HWCs with 25,000<M<1,000,000 (g/mol). Their polymer chains are built from monomeric units - nucleotides, so NA is often called polynucleotides. The peculiarity of nucleotides is that usually an “indivisible” monomeric link (for example, an amino acid residue base in proteins) is a three-component formation of an isterocyclic base, a phosphate group and a carbohydrate residue (while RNA contains ribose, and DNA contains deoxyribose).

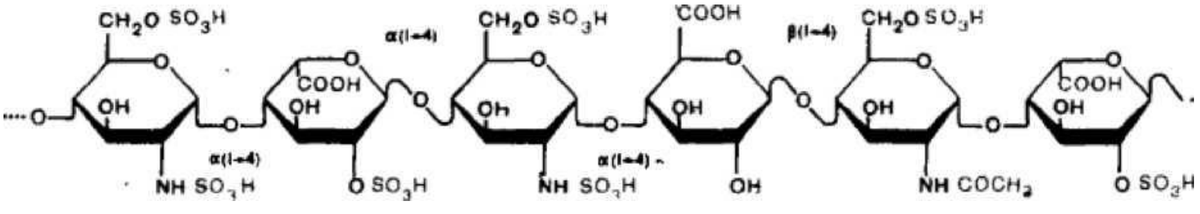
1. An example of polyelectrolytes is the structure of some connective tissue polysaccharides (skin, cartilage, cornea, joint fluid ...), which are often called acid mucopolysaccharides (from Latin mucus - mucus), because. they contain carboxyl and sulfo groups (see figures 15-17).
2.



Rice. 15. Chondroitin-4-sulfate

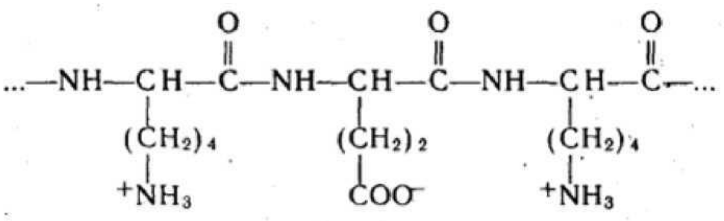


Rice. 16. Hyaluronic acid



Rice. 17. Heparin chain fragment

Connective tissue is distributed throughout the body, determines the strength and elasticity of organs, the elasticity of their connection, and resistance to infection. Connective tissue polysaccharides are associated in vivo with proteins and form proteoglycan complexes, the properties of which are determined mainly by polysaccharide components. On the whole, complexes of proteoglycan nature are polyvalent ions capable of binding K+, Na+, Ca2+ cations and thereby participating in salt metabolism.



Rice. 18. Copolymer of L-lysine and L-glutamic acid

Obviously, at low pH values (i.e., high acidity of the medium), polyampholyte molecules are positively charged; dissociation of carboxyls will be suppressed, and amino groups, on the contrary, will be stimulated. In strongly alkaline media (high pH values), polyampholyte molecules acquire a total negative charge. In a certain intermediate pH range (conditionally $3<pH<11$ for proteins), the total charge of the macromolecule will become equal to 0. This state of the protein in an aqueous solution is called isoelectric, and the pH value of the solution at which the molecule is electrically neutral is called its isoelectric point (IEP).

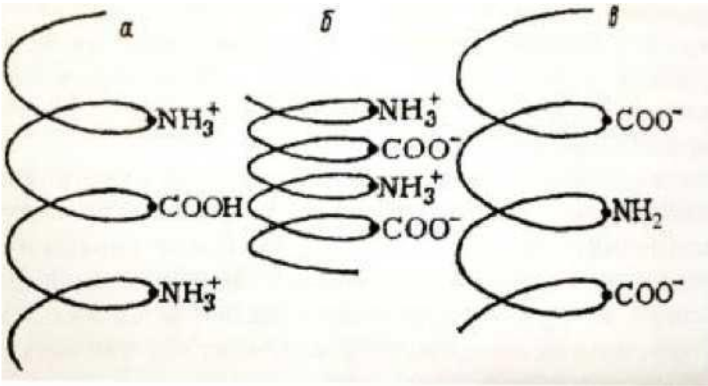
Most natural proteins contain significant amounts of dicarboxylic amino acid residues (aspartic, glutamine) in the peptide chain. Such proteins are called acidic (their IEP lies in the $pH < 7$ region). To achieve it, the protein solution must be acidified with a strictly defined amount of a strong acid in order to suppress the dissociation of some of the carboxyl groups.

Neutral proteins contain in their macromolecules an approximately equal number of acidic and basic groups and pass into an isoelectric state directly in the process of their dissolution (without the addition of a strong acid or alkali). For them pH IET ~ 7.

Molecules of basic proteins contain more KH2 groups than acidic ones. To convert them into an isoelectric state, the solution must be alkalized to deprotonate the excess basic groups. Accordingly, for them pH IEP > 7.

The shape of the protein molecule in solution depends on the reaction of the medium and the nature of the dissociation of the protein molecule. With the dissociation of ionogenic groups only according to the acidic or only according to the basic type, similar charges appear in the bent helix of the peptide chain, distributed along its entire length. Due to the emerging electrostatic forces of repulsion, the coils of the helix will move apart, and the macromolecule will stretch.

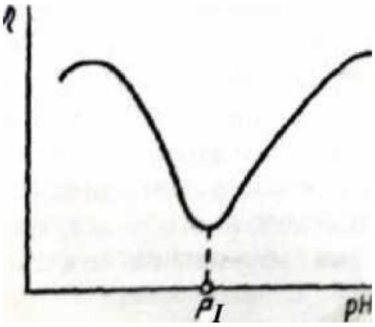
In the isoelectric state, charges of the opposite sign alternate along the peptide chain, which contributes to the compression of the molecule and even twisting it into a globule (Figure 19 b).



Rice. 19. The shape of a protein macromolecule in an acidic medium (a), at the isoelectric point (b) and in an alkaline medium (c)

This means that in the isoelectric state, protein molecules in solution occupy the leastsheath volume. As the pH increases or decreases, the molecules straighten out.

The volume of protein macromolecules affects the viscosity of their solutions. In the isoelectric state, it should be minimal (Figure 20).



Rice. 20. Dependence of the viscosity of the protein solution on the pH of the medium: p1 - pH of the isoelectric point of the protein

One of the methods for determining their isoelectric point is based on this property of protein solutions. In addition to the above, there are a number of methods for determining it:

1) according to electrophoretic mobility: the studied protein is subjected to electrophoresis in buffer solutions with different pH values; in a buffer with a pH value that matches the pH of the IEP of the protein, the latter is electrically neutral and does not move in an electric field;

2) according to the degree of coagulation: buffer solutions with different pH values are poured into test tubes, equal amounts of the studied protein are added to them and alcohol is added; the most pronounced turbidity will occur in a test tube with a buffer whose pH coincides with the pH of the IEP of the protein;

3) according to the speed of gelatinization: buffer mixtures with different pH values are poured into test tubes and a concentrated solution of the protein under study is added, gelatinization of which will occur most quickly in a solution whose pH is closest to the pH of the IEP of the protein;

4) according to the magnitude of swelling: the same amount of dry protein is poured into a series of test tubes and equal volumes of buffer solutions with different pH values are poured. The smallest swelling of the protein will be in the test tube, where the pH of the medium will be closest to the pH of the IEP of the protein.

Polyelectrolytes- these are polymers, the links of which contain functional groups capable of electrolytic dissociation (ionogenic groups). Depending on the nature of the ionic groups, polyelectrolytes, like low molecular weight electrolytes, can be strong and weak.

Salts of polyacids and polybases are generally strong polyelectrolytes.

Polyelectrolytes, the macromolecules of which contain both acidic and basic groups, are called amphoteric or polyampholytes. A typical example is a copolymer of vinylpyridine and acrylic acid:

Linear polyelectrolytes are widely used in various branches of technology as flocculants and coagulants of colloidal dispersions, for example, for clarifying waste and turbid waters, for stabilizing colloids, in particular, emulsions and foams, for structuring soils and soils. They are used in sizing, dyeing and fiber finishing, paper finishing and hardening, and are used as thickeners in the food, medical and pharmaceutical industries. Cross-linked polyelectrolytes serve as ion-exchange materials and chelators, etc.

Polyelectrolytes (polyampholytes) include such biologically important macromolecular compounds as proteins and nucleic acids.

Polyelectrolytes uniquely combine some of the most important properties of nonionic polymers and low molecular weight electrolytes. Thus, solutions of polyelectrolytes, like solutions of other polymers, have an abnormally high viscosity and, like solutions of simple polyelectrolytes, conduct electric current well. At the same time, both the hydrodynamic behavior and the electrochemical properties of polyelectrolytes in solutions are characterized by a number of features that distinguish them both from solutions of uncharged polymers and from solutions of low molecular weight electrolytes.

All the specific properties of polyelectrolytes manifest themselves only under conditions in which their macromolecules carry locally uncompensated charges. These properties are mainly determined by the interaction of the charged groups of polyions with each other and with the surrounding low molecular weight counterions. Therefore, of greatest interest are aqueous solutions of polyelectrolytes, in which the electrolytic dissociation of the corresponding functional groups that make up the links of molecular chains occurs.

Ionization equilibrium in aqueous solutions of polyelectrolytes

In a solution of a low molecular weight electrolyte, such as a weak acid, the equilibrium of the electrolytic dissociation reaction is

$$\mathbf{ON \leftrightarrow H+ + A-}$$

For low molecular weight electrolytes, the dissociation constant is a characteristic quantity. It does not depend on the concentration and degree of dissociation of the electrolyte. The picture becomes much more complicated when we consider the ionization equilibrium in a solution of a polyelectrolyte, for example, a weak polyacid, each monomeric residue of which contains one COOH group. As a result of the dissociation of this acid in an aqueous solution, a high-molecular anion and hydrogen ions are formed; its degree of dissociation $\alpha = z/P$, where z is the total charge of the macroion, P is the number of ionogenic groups, equal to the degree of polymerization. In this case, α and z are, in fact, average values, since the solution will contain particles with all intermediate degrees of ionization, from undissociated to fully ionized. Besides, the dissociation of each ionogenic group is affected by all the others, and the observed value of α will depend on a large number of different dissociation constants. If z is large, then the degree of ionization during this reaction practically does not change. The rate of the forward reaction is proportional to the concentration of macromolecules [A] and the number of carboxyl groups in the $P(1-\alpha)$ macromolecule, and the reverse reaction is proportional to the concentration of hydrogen ions, the concentration of molecules [B] and the number of carboxylate groups $P\alpha$.

Or taking into account that at $\alpha \neq 0$ and at sufficiently large P $z \gg 1$, it can be argued that macromolecules A and B are practically indistinguishable, i.e. $[A] \approx [B]$. In this regard, for the ionization equilibrium in solutions of polyelectrolytes, one can write an equation that coincides in form with the equation for a low molecular weight acid:

$$\mathbf{pH = pK + lg\,[\alpha/(1-\alpha)]} \quad \mathbf{(1)}$$

The removal of the first proton from a neutral macromolecule is described by the dissociation constant K0 of the ionogenic group that is part of the monomer unit. This value often turns out to be close to the dissociation constant of the low-molecular analog of the polyelectrolyte unit. However, for the ionization of each subsequent group of the polymer chain, it is necessary to do work against the forces of the electrostatic field created by the already charged groups. This additional work depends on the degree of ionization of the macromolecule. Therefore, the effective dissociation constant of a polyelectrolyte, in contrast to that of a low molecular weight electrolyte, also depends on the degree of its ionization.

The pK0 value is related to the energy expended on the electrolytic dissociation of an isolated –COO-H bond, and ΔpK is related to the work against electrostatic forces expended on removing a mole of charges from a mole of partially ionized coils.

The value of ΔGel depends on the ionic strength of the solution. An increase in ionic strength leads to a weakening of electrostatic interactions in the polymer chain due to partial shielding of charges and, consequently, to a decrease in ΔGel or an increase in the effective dissociation constant of the polyacid. As a result, the titration curve of the polyelectrolyte approaches the titration curve of the low molecular weight analogue. However, these curves never coincide, since even at a very high ionic strength of the solution, the interactions between the charged groups closest along the chain are not completely screened. The titration curve is also significantly affected by the structure of the polyelectrolyte chain, in particular, the configuration of the units, as well as the conformation it takes in solution. A change in the degree of polymerization (at sufficiently large P) does not affect ΔpK,

Features of hydrodynamic properties of polyelectrolytes

1. An important characteristic of the hydrodynamic behavior of solutions is their viscosity. For uncharged polymers, the reduced viscosityη decreases linearly with decreasing solution concentration, tending at extrapolation to zero concentration to its limit - intrinsic viscosity [η].

2. This makes it impossible to determine the intrinsic viscosity of the polyelectrolyte solution by extrapolating the reduced viscosity measured under such conditions to zero polymer concentration.

The increase in the reduced viscosity upon dilution of the polyelectrolyte solution is caused by the so-called. polyelectrolyte swelling, i.e. an increase in the volume and, accordingly, the linear dimensions of macromolecular coils due to an increase in the electrostatic repulsion of like-charged chain links. When a polyelectrolyte solution is diluted, the ionic strength of the solution, created by the polyelectrolyte itself, decreases. As the dilution progresses, an increasing number of compensating low-molecular counterions leave the volume of the charged macromolecular coil, forming a diffuse layer around it, which expands with dilution. The effective charge of macromolecules increases accordingly, which leads to additional swelling of macromolecular coils. It should be noted that the specific viscosity of the polyelectrolyte solution decreases upon dilution.

Polyelectrolyte swelling can be eliminated by introducing some excess of a neutral low molecular weight electrolyte into the initial solution or by maintaining a constant ionic strength of the solution upon dilution. Then the concentration of compensating counterions in molecular coils does not change upon dilution, and the polyelectrolyte in solution behaves like an uncharged polymer: the reduced viscosity decreases linearly with decreasing concentration. A similar behavior is exhibited by a polyelectrolyte in solvents with a relatively low dielectric constant, in which electrolytic dissociation is almost completely suppressed, for example, in absolute methanol or dioxane. Such dilution techniques or the selection of a suitable solvent are used in determining the molecular weight of a polyelectrolyte by the viscometric method.

Of greatest interest is isoionic dilution, i.e. dilution at a constant ionic strength of the solution. To maintain a constant ionic strength, it is necessary to compensate for its decrease upon dilution by introducing a certain amount of a low molecular weight electrolyte into the solution. The total effective ionic strength of the solution I is determined by the contributions of the low molecular weight electrolyte Inme and the polyelectrolyte Ipe:

$$I = I_{nme} + Ipe$$

The complexity of maintaining the constancy of the ionic strength lies in taking into account the contribution of the polyelectrolyte. If the polyelectrolyte is strong, i.e. each monomer unit carries an ionized group, then

$$\boldsymbol{I_{pe}=C\varphi}$$

where C is the concentration of the polyelectrolyte (base mol/l); φ is the fraction of "intrinsic" counterions that are not bound inside the coil.

Usually $\varphi < 1$, since some of the counterions are always strongly held by polyions. An aqueous salt-free solution of a polyelectrolyte with a concentration of C0 is diluted with a solution of a neutral low-molecular salt of a constant concentration $\chi\infty$. If, in this case, the ionic strength of the solution is greater (less) than the ionic strength of the initial polyelectrolyte solution, then the dependence of the reduced viscosity on the concentration is expressed by a concave (respectively, convex) curve (see Fig. 2). In practice, dilutions are made with salt solutions of various concentrations until a straight-line relationship is obtained. This means that the ionic strength of the solution remains constant during dilution, and the selected concentration of the low molecular weight electrolyte is exactly equal to the ionic strength of the initial polyelectrolyte solution, i.e.

Using this equation, one can determine the proportion of free counterions in the solution and the proportion of counterions (1 - φ) bound by polyions. The fraction of bound counterions depends on the molecular weight and charge of the polyelectrolyte, but is practically independent of the polymer concentration and the ionic strength of the solution.

Lecture 25.

Ionic equilibrium in polyelectrolytes

In a solution of a low molecular weight electrolyte, such as a weak acid, the equilibrium of the electrolytic dissociation reaction

$$HA \rightleftharpoons H^+ + A^-$$

is described by the equation

$$[H^+]\alpha/1-\alpha = K' \text{ или } pH = pK` + lg\alpha/1-\alpha$$

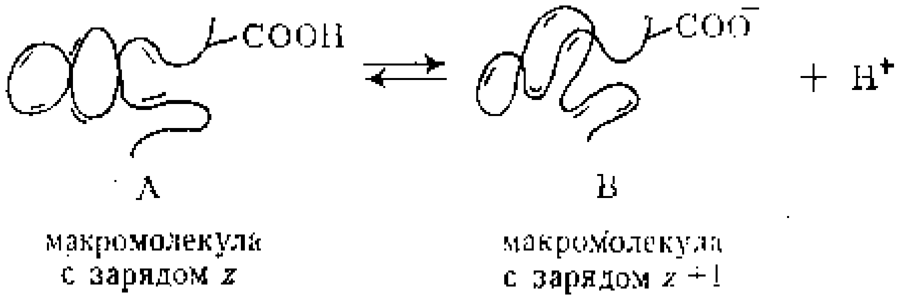
where K' is the electrolytic dissociation constant; □ degree of dissociation (ionization).

Strictly speaking, the dissociation constant K' at a finite ionic strength is an effective quantity. The true constant $K = K'\gamma_{A^-}/\gamma_{HA}$ (where γ_{A^-} and γ_{HA} are the activity coefficients of the corresponding particles). However, since the ratio of the activity coefficients is usually close to unity, it can be assumed with a good approximation that $K' \approx K$, i.e., that the effective constant describes the behavior of a low molecular weight electrolyte in an aqueous solution quite well. For low molecular weight electrolytes, the dissociation constant is a characteristic quantity. It does not depend on the concentration, the degree of dissociation of the electrolyte and is related to the change in the standard Gibbs energy of molecular ionization (ΔG^0_{ion})) by the equation

polyelectrolyte polybase solution ionization

$$pK_0 = 0.434\Delta G^0_{ион}/RT$$

Let us consider the ionization equilibrium in a solution of a polyelectrolyte, for example, a weak polyacid containing P ionogenic groups in the macromolecule. If there is one ionogenic group in each monomer unit, then P coincides with the degree of polymerization. The degree of dissociation of such a polyelectrolyte is, generally speaking, determined by various dissociation constants. For example:



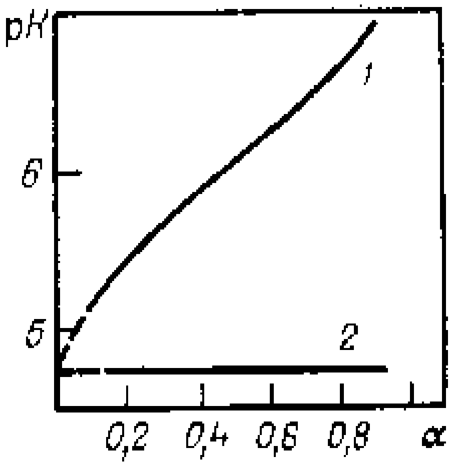
If z is large, then the degree of ionization during this reaction practically does not change. The rate of the forward reaction is proportional to the concentration of macromolecules [A] and the number of carboxyl groups in the macromolecule (1-α)P, and the reverse reaction is proportional to the concentration of hydrogen ions, the concentration of macromolecules [B] and the number of carboxylate groups □P. Thus, the equilibrium constant

$$K = \frac{[H^+][B]\alpha P}{[A](1 - \alpha)P}$$

Or taking into account that at $\alpha \neq 0$ and at sufficiently large P $z >> 1$, it can be argued that macromolecules A and B are practically indistinguishable, i.e. [A] ~ [B]. In this regard, for the ionization equilibrium in solutions of polyelectrolytes, one can write an equation that coincides in form with the equation for a low molecular weight acid.

$$pH = pK` + lg\alpha/1-\alpha \quad (1)$$

The removal of the first proton from a neutral macromolecule is described by the dissociation constant K0 of the ionogenic group that is part of the monomer unit. This value often turns out to be close to the dissociation constant of the low-molecular analog of the polyelectrolyte unit. Such ionization corresponds to the standard change in the Gibbs energy □G0ion. However, for the ionization of each subsequent group of the polymer chain, additional work must be done against the forces of the electrostatic field created by the already charged groups. This additional work depends on the degree of ionization of the macromolecule. Therefore, the effective dissociation constant of a polyelectrolyte, in contrast to that of a low molecular weight electrolyte, also depends on the degree of its ionization (Fig. 1).



In some cases, the ionization of a polyelectrolyte in a certain range of K_0 ΔG^0 may be accompanied by a cooperative conformational transition of molecular chains, i.e., a rather sharp change in the shape of macromolecules in solution. Then the value ΔG^0 includes not only the electrostatic component of the Gibbs energy of the polyelectrolyte, but also the energy of the conformational transition. If the conformational transition occurs in a fairly narrow range of pH values (or □), then these two components can be separated and the thermodynamic parameters of the corresponding conformational transition can be determined from the potentiometric titration curves.

Chemical properties of polymers

Polymers are prone to various chemical reactions, which result in a change in the chemical structure or degree of polymerization of macromolecules.

The chemical reactions of macromolecular compounds do not differ in nature from the reactions of classical organic chemistry, but the large size of macromolecules and the complexity of the structure introduce features into these interactions.

They depend on the composition, molecular weight and structure of macromolecules. Polymers are characterized by structuring and degradation reactions. Structuring of polymers is the "crosslinking" of molecules, i.e. the formation of cross chemical bonds between macromolecules.

Examples.

1. Vulcanization of rubber by adding sulfur when heated.

2. At a low temperature, the polymer is in a glassy state (region I), in which the polymer behaves like an elastic body (where there is no movement, both of the entire molecule and of individual links, and there are only vibrations of atoms around the equilibrium position).

As a result of the interaction of rubber with sulfur (0.5–5%), soft, sticky rubber turns into elastic, elastic rubber or hard ebonite (20% sulfur or more) with a spatial mesh structure.

Interaction of molecules with each other or with low molecular weight substances due to functional groups (during curing of thermosetting resins, halogenation of polyolefins, hydrolysis of polyacryls).

Chemical properties depend on the composition, molecular weight and structure of polymers. They are characterized by cross-linking reactions of macromolecules, interactions of functional groups with each other and with low molecular weight substances, and destruction. The presence of double bonds and functional groups in macromolecules causes an increase in the reactivity of polymers. For the same reason, individual macromolecules can be cross-linked. Examples of cross-linking can be vulcanization and translation of linear macromolecules of thermosetting polymers into network structures. During vulcanization, rubber interacts with a vulcanizing agent, usually sulfur, with the formation of rubber (0.5 - 5% sulfur) or ebonite (20% or more sulfur).

The reactions of interaction of functional groups with low molecular weight substances include halogenation of polyolefins, hydrolysis of polyacrylates, etc.

Polymers can be subject to degradation, i.e. destruction under the influence of oxygen, light, heat and radiation. Often, destruction is caused by the simultaneous action of several factors. As a result of degradation, the molecular weight of macromolecules decreases, the chemical and physical properties of polymers change, and eventually the polymers become unsuitable for further use. The process of deterioration of the properties of polymers over time as a result of the destruction of macromolecules is called the aging of polymers. To slow down the degradation, stabilizers, most often antioxidants, are introduced into the composition of polymers; oxidation reaction inhibitors (phosphites, phenols, aromatic amines). Stabilization is usually due to chain termination during the interaction of antioxidants with free radicals formed during the oxidation reaction.

Mechanical properties of polymers. Mechanical properties are determined by the elemental composition, molecular weight, structure and physical state of macromolecules.

Polymers are characterized by some features, such as a highly elastic state under certain conditions, mechanical glass transition, and the ability of thermosetting macromolecules to form rigid network structures. The mechanical strength of polymers increases with an increase in their molecular weight, during the transition from linear to branched and further network structures. Stereo-regular structures have higher strength than disordered polymers. A further increase in the mechanical strength of polymers is observed upon their transition to the crystalline state. For example, the tensile strength of crystalline polyethylene is 1.5-2.0 orders of magnitude higher than that of amorphous polyethylene. The specific strength per unit cross-sectional area of crystalline polymers is comparable, and per unit mass is an order of magnitude higher than the strength of alloyed steels.

The mechanical strength of polymers can also be improved by the addition of fillers, such as carbon black and chalk, reinforcement with fibers, such as fiberglass.

Electrical properties of polymers. All substances are divided into dielectrics, semiconductors and conductors.

Dielectrics have very low conductivity (s<10-8 ohm -1×cm -1), which increases with increasing temperature. Under the action of an external electric field, dielectrics are polarized, i.e. certain orientation of the molecules. Due to polarization inside the dielectric, its own electric field arises, which weakens the effect of the external field. A quantitative characteristic of the weakening of the external field is the dielectric constant, showing how many times the force of interaction of two charges in a dielectric is less than in vacuum. Due to polarization in the dielectric, dielectric losses arise, i.e. e transformation.

Organic semiconductors and electrolytes. Semiconductors include substances whose electrical conductivity lies within 10-10¸10-3 Om-1× cm-1. The electrical conductivity of semiconductors increases with increasing temperature and when exposed to light. Some polymers have semiconductor properties. Usually these are polymers with a system of conjugated double bonds. The semiconductor properties of such polymers are due to the presence of non-localized n-electrons of conjugated double bonds.

In an electric field of a certain voltage, these electrons can move along the circuit, providing charge transfer. Examples of organic semiconductors are polyacetylene [-CH=CH-]n, polyvinylenes [-HC=C-]n, polynitriles [-N==C-]n, R R polyacrylonitrile heat treatment products

In recent years, the phenomenon of a sharp increase in the electrical conductivity of polyacetylene, polyaniline (-C6H3NH2-) n, polypyrrole (-C4H3N-) n, and other polymers during their chemical or electrochemical oxidation or reduction has been discovered. During electrochemical oxidation, anions, for example ClO4-, are introduced into the polymer composition, during reduction - cations, for example Li+. At some

Reactivity of functional groups

1. Reactions not accompanied by a change in the degree of polymerization:

a) polymer analogous transformations;

b) intramolecular reactions.

2. Reactions leading to a change in the degree of polymerization:

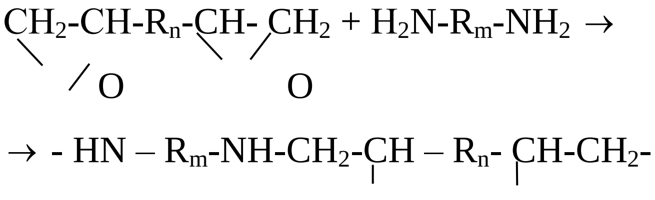
a) reactions proceeding with an increase in molecular weight (crosslinking reactions);

b) reactions proceeding with a decrease in molecular weight (destruction reactions).

Let us dwell in more detail on the second type of reactions, since it is most often implemented in the production or operation of polymeric building materials.

Cross-linking reactions of macromolecules are called cross-linking reactions or structuring. They occur under the action of crosslinking agents on the polymer or under the influence of heat, light, radiation.

Cross-linking processes are widely used in industry, for example, in the vulcanization of rubbers, the curing of plastics, and the drying of paint coatings. For example, curing epoxy resins:



$$\underbrace{CH_2-CH}_{O}-R_n-\underbrace{CH-CH_2}_{O} + H_2N-R_m-NH_2 \rightarrow$$

$$\rightarrow -HN-R_m-NH-CH_2-\underset{|}{CH}-R_n-\underset{|}{CH}-CH_2-$$

OH OH

During the operation of products made of polymeric materials under the influence of the environment, their gradual destruction (aging) occurs - destruction. Destruction reactions are called reactions that proceed with breaking the bonds of the main molecular chain and leading to a decrease in the molecular weight of the polymer without changing its chemical composition.

The consequences of these processes are changes in the physico-chemical and physico-mechanical properties of polymeric materials (i.e. they gradually become unusable), the release of low-molecular degradation products, which in some cases are toxic.

The destruction of polymers can proceed under the action of chemical agents and physical impact. Depending on the nature of the impact, destruction is classified into chemical (impact of water, acids, alkalis, alcohols), highlighting oxidative (exposure to oxygen), mechanical, thermal and photodestruction (under the influence of light). Knowledge of the mechanism and basic patterns of the processes of polymer degradation is necessary to regulate this reaction (in the case of the operation of polymeric building materials, minimizing it).

One of the most destructive types of degradation is oxidative. An example of an oxidative degradation process without taking into account the mechanism:

$$-CH_2-CH=CH-CH_2- \xrightarrow{O_2} -CH_2-CH=O + O=CH-CH_2-$$

Oxidative degradation of polymers (under the action of oxidizing agents) proceeds, as a rule, by a chain radical mechanism, like many other types of degradation.

Like any chain reaction, oxidative degradation consists of several stages: initiation, chain growth, and chain termination. The main stages of the oxidation reaction of organic polymers. At present, a large number of methods for inhibiting the oxidation process (oxidative stabilization of polymers) are known. These methods include:

- selection of optimal processing conditions;

- adding special substances to the polymer, stabilizers - antioxidants or oxidation inhibitors;
- regulation of the supramolecular structure of the polymeric material;
- deactivation of impurities that catalyze the chain nucleation reaction;
- reduction of oxygen concentration in the polymer.

Lecture 27.

Intermacromolecular reactions

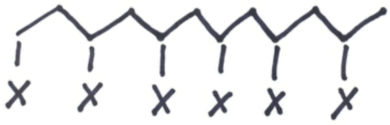
One of the possible ways to synthesize polymers containing functional groups in their structure is the chemical modification of polymers containing reactive groups.

In many cases, the synthesis of reactive polymers is an independent task, as, for example, in the preparation of ion exchange resins from conventional polymers.

Chemical modification significantly expands the scope of natural and synthetic polymers, giving them new properties. Often, with the help of chemical modification, polymers are formed that cannot be obtained by polymerization or polycondensation.

Chemical modification of polymers can be carried out both at the stage of their synthesis (before isolation from solution or latex), and directly during the processing of polymers into the corresponding products (rubber vulcanization) or already in the product (chemical surface modification, crosslinking).

In functional polymers, reactive groups can be regularly:



or statistically:

Distributed along the chain of the macromolecule, and in some cases they are end groups:

The reactivity of polymers varies depending on the concentration of the respective groups.

Chemical modification of polymers is carried out by conducting various chemical reactions of polymers, the whole variety of which can be divided into the following main groups:

- reactions of polymers with low molecular weight reagents;
- including polymer-analogous transformations;
- destruction;
- stitching;
- reactions of macromolecules with each other.

Functional polymers can be synthesized by all known methods of obtaining polymers: polymerization, copolymerization, graft and block polymerization, polycondensation and copolycondensation, as well as polymer-analogous transformations.

Lecture 28

Destruction of polymers

Plan:

1. Reactions leading to a decrease in the degree of polymerization.
2. Destruction. Destruction under the influence of chemical agents.
3. Physical destruction. destruction mechanism.
4. Aging of polymers.
5. Destruction under the influence of air, rays, radiation.

Destruction(from Latin destructio - destruction) - the general name of the processes that occur with the breaking of chemical bonds in macromolecules and lead to a decrease in the degree of polymerization or molecular weight of the polymer, therefore, to a change in the properties of the polymer.

Depending on the place of bond breaking, degradation is distinguished in the main and side chains of polymers.

*destruction*It is customary to classify according to external, causing it, factors.

There are thermal, photochemical, oxidative, radiation, mechanical, etc. degradation. Polymer degradation is often caused by the simultaneous action of several factors. For example, heat and oxygen lead to thermal-oxidative degradation. Destruction is often referred to as the total amount of transformations occurring in a polymer under the action of external factors.

Destruction is one of the reasons for the aging of polymers. As a rule, it is a chain process and includes the following main stages:

– initiation, i.e. formation of active centers;

- continuation or development of the chain (a set of reactions involving active centers, leading to a change in the chemical structure and physical properties of polymers);

– chain termination (processes of deactivation of active centers).

Thermaldestruction occurs under the action of high temperatures (230–430 ° C) in the absence of oxygen. The process in most cases proceeds by a radical - chain mechanism. Its main stages can be considered on the example of polyethylene. Initiation (the slowest stage) is carried out as a result of thermal decomposition of the macromolecule with the formation of macroradicals:

Chain termination occurs when two radicals interact:

Depending on the ratio of the rates of individual stages, thermal degradation produces different amounts of monomer and products with a lower molecular weight than that of the initial polymer, and deep degradation often results in coke.

An example of a complex process that includes radical, ionic and molecular reactions is the thermal destruction of PVC.

To make the polymers stable to thermal degradation, antioxidant and stabilizer additives are introduced into them. Stabilizers should not change the physical properties of the polymer and are introduced in an amount of no more than 2%.

Photochemical degradation(photolysis) is caused by light absorbed by the chromophore groups of the polymer, the products of its thermal or thermo-oxidative transformation and (or) impurities.

During photolysis, in addition to breaking chemical bonds, "crosslinking" occurs, the formation of double bonds and free radicals. The process is characterized by the quantum yield of chain breaks (the number of breaks per absorbed light quantum), which for various polymers lies in the range of 10-4–10-1.

*Radiation destruction*is caused by hard ionizing radiation (α, β, γ - radiation), accelerated electrons and ions. Under the action of high-energy radiation, excitation occurs, that is, the transition of electrons to a higher energy level, and ionization associated with the ejection of electrons. In this case, macromolecules lose their stability, destruction is facilitated. Depolymerization does not occur. Sometimes low-molecular gases (hydrogen, chlorine, methane, $CO2$, etc.) are released. The main process is the elimination of hydrogen and small side groups, for example, $CH3$, $C2H5$.

Due to the high concentration of free radicals in relatively small areas of the substance, this destruction is accompanied by cross-linking of macromolecules, which in most cases prevails over the destruction itself.

Mechanical destruction(mechanochemical) proceeds under the action of constant (static) and variable mechanical loads on solid polymers that exceed the strength limits of these materials or when polymer melts and solutions are mixed. The first stage of this destruction is the rupture of the polymer chain under the action of stresses:

Further, the same processes can occur in the polymer as during thermal degradation.

The action of chemicals on polymers leads to oxidative ($O2$) or chemical degradation ($O3$, water, acids, alkalis, $Cl2$, etc.). The latter is subdivided into ozone, hydrolytic, etc.

*Oxidative (or thermo-oxidative) degradation*is a multi-stage chain reaction. Main stages:

1. Initiation (chain initiation): $RH + O2 \rightarrow R^{\bullet} + HO2^{\bullet}$ (where RH is a polymer monomer unit, for example, $\sim CH2 - CH2 \sim$).

Chain development: $R^{\bullet} + O2 \rightarrow RO2^{\bullet}$. In some cases, at temperatures above 200 0C, the process is complicated by the decomposition of the peroxide radical $RO2$.

2. Chain termination occurs as a result of recombination and disproportionation of radicals, mainly peroxide ones ($2RO2^{\bullet} \rightarrow ROOR + O2$). During the decomposition of ROOR peroxides, some of the radicals are regenerated. An important role in chain termination is played by low molecular weight radicals ($HO2^{\bullet}$, $HO^{\bullet}$, etc.). The rate of thermal-oxidative degradation is usually higher than that of thermal degradation. With the simultaneous action of light and oxygen, photooxidative degradation occurs, in which the nucleation and branching of the chain are photochemical processes. Branching can occur due to photolysis of hydroperoxides and the formation of new chromophore groups (for example, ketone, ketoimide).

*Ozone destruction*accompanied by oxidative processes. Due to the high reactivity of ozone, it flows in the surface layers of the polymer, in which deep transformations occur, leading to cracking.

biological destruction. Microorganisms, insects, rodents act on a number of products made of polymers and destroy them. Destruction is caused by enzymes secreted by these organisms.

The most common cause of biological degradation of polymers are microorganisms, the main of which is mold. Microorganisms worsen the hygienic properties of products, their appearance. Pigments formed by microorganisms color polymers, even after removing the culture, traces remain on the material in the form of spots of gray, green, black. Mold contributes to the condensation of water vapor, worsens the mechanical and other properties of materials. Metabolites, including enzymes, can cause degradation of the polymer itself, resulting in loss of gloss or surface etching. Some types of mold and bacteria have the ability to use the constituent parts of polymers (plasticizers, fillers, and others) for nutrition, accelerating the destruction of products. For example, vinyl chloride films plasticized with dibutyl sebacate,

Most natural macromolecular compounds or their derivatives are a source of nutrition for microorganisms. On the contrary, most genuinely synthetic polymers are not a source of food for microorganisms, and the growth of the latter is impossible. These materials themselves do not possess fungistatic (capable of inhibiting the reproduction of microorganisms) and fungicidal (capable of killing microorganisms) properties; additions to them of substances “edible” for microorganisms can contribute to their destruction. Such additives can be fillers, plasticizers. Therefore, the problem of the stability of these polymeric materials is solved as the problem of the stability of fillers, plasticizers, etc.

Chemical degradation- this is the interaction of polymeric materials with the environment, causing their corrosion.

Unlike low molecular weight organic substances, macromolecules contain a large number of reactive groups. However, individual groups evenly participate in reactions not only within a given molecule, but also in different molecules.

When classifying with respect to chemically aggressive media, polymers are divided into two groups: heterochain (the main chain contains oxygen, nitrogen, sulfur, etc.) and carbochain, in which the chains are formed only by carbon atoms.

Heterochains (polyamides, thiokols, siloxanes, polyesters) easily decompose under the influence of hot water, acids, alkalis.

Carbochain polymers are more resistant to aggressive media. They are divided into three groups.

*Medium resistant polymers*with the structure of saturated hydrocarbons (polyethylene, polypropylene, polyisobutylene) and other polymers with the structure of saturated hydrocarbons with substituents and structural elements; increasing resistance to aggressive environments. Such substituents are fluorine (polytetrafluoroethylene), chlorine (trifluoroethylene), benzene rings (polystyrene). These polymers are resistant to acids, weak oxidizing agents, and fluorine-substituted polymers are also resistant to strong oxidizing agents.

Polymers containing structural elements that reduce their resistance to aggressive media(for example, double bonds that easily interact with oxygen, halogens, acids, OH groups, CH3COOH, etc.).

Aging of polymers- a process in which, under the influence of various factors, the composition and structure of polymer molecules change over time. As a result of aging, the mechanical, electrical, and optical properties of polymers usually deteriorate.

There are two types of polymer aging - degradation, in which long chains of polymer molecules are split, and structuring - the formation of a three-dimensional polymer.

The aging of polymers at high temperatures in the absence of oxygen is commonly referred to as thermal degradation.

The aging of polymers is significantly accelerated in the presence of oxygen, air, heat, light, as well as under the influence of various aggressive liquids or gases, such as acids, alkalis, gaseous chlorine. In all cases, destruction may be accompanied by structuring. During degradation, the molecular weight usually decreases, and during structuring, it increases. Stabilizers and antioxidants are added to polymers to slow down aging.

Lecture 29

Methods for stabilizing polymers

Plan:

1. Substances that accelerate and slow down destruction.
2. Methods for stabilization of polymers.
3. Stabilizers and requirements for them.

The weldability of plastics largely depends on their structural properties. Therefore, in order to select the appropriate welding technology, it is necessary to know the composition, structure and properties of plastics.

Plastics- These are a variety of materials obtained on the basis of synthetic or natural polymers. Various additives are introduced into polymers: stabilizers, plasticizers, fillers, dyes.

*Stabilizers*serve to increase the resistance of polymers when exposed to light, elevated temperatures and other factors.

plasticizers- to improve technological and operational properties.

Fillers- to increase strength, improve dielectric and other properties, to reduce the consumption of polymer resin.

The properties of plastics are determined by their base - the polymer. The basis of plastics are macromolecular compounds, which consist of giant molecules of a linear, branched or spatial structure.

Plastics with a linear structure of macromolecules are characterized by high strength, significant elasticity and the ability to highly elastic deformations (natural or artificial rubber, polyethylene, polystyrene).

In polymers with a branched structure, strength and heat resistance decrease (phenol-formaldehyde, polyester).

Plastics with a spatial structure of molecules are characterized by complete insolubility, lack of elasticity and plasticity at elevated temperatures, high hardness and brittleness (synthetic resins in the final stage of shaping).

Linear and branched polymers serve as the basis for thermoplastic plastics (thermoplastics). Thermoplastics are produced on the basis of polymers, the molecules of which are bound by weak intermolecular forces. The presence of such intermolecular bonds allows the polymer to repeatedly soften when heated and harden when cooled, without losing its properties.

*Thermoplastics*are obtained on the basis of polymers, the molecules of which, along with intermolecular forces, can be chemically bonded. Chemical bonds occur when heated or the introduction of a hardener. When chemical bonds occur, the polymer turns into a rigid non-melting and insoluble substance (textolite, ebonite, bakelite).

Plastic welding isthe process of permanent connection of thermoplastics and thermoplastics, as a result of which the interface between the parts to be joined disappears.

The connection of thermoplastics is carried out by a method based on the chemical interaction between the surfaces directly or with the participation of a filler material (the so-called chemical welding). The implementation of this method requires intensive heating of the surfaces and intensification of the oscillations of the links of the polymer molecules by current or ultrasound.

Further in the work we will talk about welding thermoplastics.

Thermoplastics are welded using heat. Depending on whether heat sources are used directly or whether various types of energy are converted into heat, thermoplastic welding methods are divided into two groups.

The first type of welding includes hot element welding, hot air (gas) welding, extrusion and injection welding. To the second - electrical connection, ultrasonic and high-frequency welding, friction welding, etc. A distinctive feature of plastic welding is that the connection process occurs at a temperature above the softening temperature, but below the decomposition temperature in the viscous-flow state of the polymer under pressure.

Lecture 30

Small-tonnage polymeric materials.

Plan:

1. Polymer composite materials.
2. Basic concepts about polymers with specific properties.
3. Polymers in nanotechnology.

Production of low-tonnage polymers

It is known that today there are many polymeric materials that are produced in large quantities. These are mainly polymer plastics, rubbers, heat-resistant polymers, polymer coating materials and so on. However, little is known about polymeric materials and tools, which are rarely produced.

Based on low-productive polymeric materials:

1. Polymer adhesives;
2. Polymeric materials with biologically active properties;
3. Smart polymers;

4. Includes polymers used in medicine.

Low-tonnage polymer materials produced in the state of Posia. This is 5%, and now it is in the spotlight in Uzbekistan.

Polymer composite materials

In addition to the main polymeric component, composite materials containing components that combine or modify components are widely distributed in nature and have been known for a long time. Any modern design or building material consists of a composition. These are not individual high-molecular compounds, but polymers - in addition to binders, fillers, stabilizers, pigments, etc., it is fully compatible with polymeric materials; fillers can be solid, liquid or gaseous (in the form of foam).

The greatest stability effect is achieved when forming a monomolecular membrane, since the orienting movement of the filler surface decreases with increasing distance, and in practice, macromolecules do not spread beyond the first layer. If the filler is present in sufficient quantity, a highly oriented bimolecular membrane is formed between the particles.

Thus, an increase in the mechanical strength of the polymer when a filler is added to the composition is associated with a decrease in the thickness of the polymer layer and adhesion forces due to the orientation of macromolecules and the strengthening of the polymer. Due to adhesive forces up to 3000 kg / cm2, the technical strength of each component in the composition is higher.

Of great importance are the structure of the filler (anisotropic, fibrous, layered) and other factors that determine the mechanical properties of the composition. Therefore, in the case of easily degradable graphite-containing rubbers, talc is rarely added to the polymer, which enhances the effect of the filler, despite its high adhesion. On the contrary, fillers such as fabric, wadding, veneer, paper and other layered and fibrous materials have a very strong reinforcing effect.

In practice, compositions of polymers and heavy-duty fibers (fiberglass, chemical and synthetic fibers, fabrics, graphite fibers with greater strength than steel, etc.) are widely used - reinforced plastics.

Reinforcing fillers such as alumina single crystals, silicon, boron, graphite carbides, etc., which have a higher specific strength (strength to density ratio) than steel and glass fibers, are of great importance in terms of obtaining materials with high mechanical strength.

Reinforced plastics can combine the characteristic, flexible, high-strength properties found in fibrous materials specific to polymers; in which the fiber acts as a reinforcing material and the polymer acts as a binder to transfer stress during specimen deformation. In this way, the binders allow all the fibers to work simultaneously, which together increases the tear resistance.

Nonwovens resembling reinforced plastic are important; in the production of some of them, labor-intensive processes such as spinning and weaving are replaced by gluing fibers together with polymer solutions and dispersions.

In conclusion, fillers can not only increase the mechanical strength of polymeric materials, but also significantly affect their other properties. For example, the use of asbestos makes it possible to manufacture products resistant to temperatures up to 10,000 °C in a short time; some fillers (usually activators) increase the abrasion resistance of polymer materials, while others reduce their flammability by increasing heat resistance.

Metal-filled polymers (metal polymers) formed when powdered metals or metal fibers (aluminum, nickel, steel, tin, cadmium, beryllium, boron, tungsten, titanium, lacquered iron, copper, magnesium, etc.) are used as fillers have great importance. Such metallic polymers are characterized by high strength (especially when used in the form of fibers), heat resistance, thermal conductivity and electrical conductivity. In some cases, strength depends not only on physical impact, but also on the chemical interaction of the polymer with the metal (formation of complexes due to bond electrons, reaction of carboxyl groups with oxides on the metal surface, etc.).

Special polymeric materials.

polymer adhesives. polymer preparations.

Polymer adhesives mainly include epoxies, cyanoacrylates, polyurethanes, silicone resins. To obtain such polymeric materials, the starting polymer must be very pure.

Smart polymers include biologically functional functional polymers. These include water-soluble polymers, artificial enzymes, and artificial organs (insulin, ribonuclease). The industry produces more than 20 enzymes, prolongation drugs, artificial kidneys, heart valves, blood vessels, and artificial skin. In addition, anion exchangers, cation exchangers, fibrous polymers are produced.

Deep fundamental work is being carried out in this direction in Uzbekistan. Academicians O.S. Sodikov, S.Yu. Yunusov and their school are among the world famous scientists who contributed to the development of the chemistry of alkaloids and the chemistry of synthetic physiologically active substances.

To date, the range of drugs from synthetic and natural substances in the CIS countries has exceeded 140 thousand. Nevertheless, the need for medicine is growing. In particular, there are still not enough drugs that have less adverse effects on the body, can selectively affect the body, are administered in small amounts, have a long-term physiological effect, and can satisfy the delicate requirements of such medicine. That is why certain branches of chemistry are devoted to improving the properties of drugs, increasing their effectiveness, expanding their range, and discovering therapeutic agents with new properties. One such new field of chemistry is high molecular weight chemistry. But really high-molecular substances (polymers) have served as medicine since ancient times. Amber, natural polymer,

Polymers in ophthalmology

The demand for vision correction has grown significantly in recent years. Therefore, instead of glasses, various medical lenses were invented.

With the advent of plastics, polymer contact lenses began to be used in this area as well. In the early 1950s, contact lenses made of polymethyl methacrylate had good physiological properties and a number of advantages, which were called "hard" lenses. In the early 1970s, polyacrylate-based hydrogel contact lenses began to be referred to as "soft" lenses. There are currently 5.5 million people living in the United States. pieces of "soft" lenses and 3 million pieces. pieces of "hard" lenses were made.

Polymers in dentistry

The field of dentistry in medicine has also developed rapidly since the advent of polymer dentures and dentures. Resins used in dentistry must have high hardness, be strong, non-abrasive, odorless, easy to disinfect, and have a color that matches the color of the skin of the mouth. Such prostheses are usually made of a polymer consisting of two or three monomers, and it is difficult to see in their artificiality.

Polymers as binders

White transparent polyurethane adhesive material is widely used.

With the help of this connective tissue, the wound heals faster and the tissue grows faster. After applying the bandage, it does not need to be quickly changed, as the wound is visible.

Polymers in nanotechnologies. Smart polymers

Problems of studying polymers over time:

Before 1980: polymers as building materials (plastics, rubbers, fibers, films, adhesives, etc.).

After 1980: polymers as functional materials (supersorbents, conductive polymers, polymers in optics, medicine, etc.)

Post-2000: "smart" (stimulus-sensitive) polymers (polymers that perform different functions depending on changes in the environment).

"Smart" polymers are materials that can change their properties based on changes in the external environment (ambient pH, temperature, ionic strength, light, electric field, magnetic field, etc.) that occur in the system. These changes can be detected with the naked eye (formation of a new phase in a homogeneous solution, increase or decrease in the degree of hydrogel swelling, etc.).

Existeven specialized journals such as the Journal of Intelligent Material Systems and Structures, Technomic Publishing and others.

DESCRIPTION OF LABORATORY WORKS

Laboratory work №1

Study of the kinetics of styrene polymerization

Purpose of work: to study the features of the course of the process of radical polymerization in a monomer medium and to evaluate the influence of various factors on the kinetic parameters of the reaction.

The content of the work:

To study the influence of a number of factors on the rate of radical polymerization of styrene in bulk (time, temperature, concentration of the initiator) and evaluate the contribution of each factor, as well as find the order of the reaction according to the initiator and calculate the total activation energy of the process.

Equipment and reagents:

Reagents: styrene, benzoyl peroxide.

Instruments and utensils: refractometer, thermostats for temperatures from 20 to 80 ° C, test tubes with ground stoppers with a capacity of 20-25 cm3, weighing bottles (3 pcs.), Beakers with a capacity of 100 cm3 (3 pcs.), 10 cm pipettes, syringe with long needle, spatula, watch glass.

Operating procedure:

Receive a task from the teacher according to the table of options (Table 1.1).

Table1.1

Task Versions

№	Factor values			
	T, °C	content of initiator, % ″of monomer weight)		
		C_1	C_2	C_3
1	65	0, 2	0, 7	1, 2
2	80	0, 2	0, 5	1, 0
3	75	0, 2	0, 3	0, 8
4	60	0, 2	1, 0	1, 5

The temperatures of the test tubes are measured every 10 minutes. The refractometric method for determining the polymer yield is based on measuring the refractive index of the reaction mixture during polymerization, the values of which are different for the monomer and polymer. Before starting measurements of the refractive index, the refractometer is thermostated at 20 ° C for 10-15 minutes. Measuring the refractive index in samples of the reaction mixture (see Section 3) is determined using Table. 1.2 polymer yield (x) at the time of sampling. Obtained values are entered in the table. 1.3.

Table 1.2

Dependence n^{20}_{D}| from polymer output

polymer yield x, %	n_D^{20}	polymer yield	n_D^{20}	polymer yield	n_D^{20}
0	1, 5420	11	1, 5475	21	1, 5518
2	1, 5429	12	1, 5482	22	1, 5520.
3	1, 5435	13	1, 5488	23	1, 5523
4	1, 5441	14	1, 5492	24	1, 5525
5	1, 5446	15	1, 5495	25	1, 5528

6	1,5451	16	1,5500	26	1,5531
7	1,5455	17	1,5504	27	1,5534
8	1,5461	18	1,5508	28	1,5537
9	1,5465	19	1,5511	29	1,5540
10	1,5468	20	1,5515	30	1,5543

Table 1.3

Results Recording Form

Loading, gr		Concentration of initiator [I], % (мас.)	Polymerization time t, min	n_D^{20}	Polymer yield (x)	
monomer	initiator				%	gr

Safety precautions:

Styrene is a flammable hydrocarbon, so the same precautions must be observed when handling and storing it. as when working with other flammable liquids (benzene, toluene, etc.). Explosive concentrations of styrene in a mixture with air at atmospheric pressure and a temperature of 29.3-65.3 ° C are in the range from 1.1 to 6.1% (volume). When working with styrene, open flame, friction and static electricity should be avoided.

Styrene vapors are moderately toxic by inhalation. The sweet smell of the monomer and the unpleasant pungent odor due to the presence of aldehydes are readily recognized long before toxic concentrations of monomer vapor are reached. Irritation of the mucous membranes of the eyes and nose is also felt before reaching dangerous concentrations already at 6.0-6.3 mg / l.

Dangerous concentrations of styrene vapors in the air are 10-12 mg/l, acting for 8 hours, or a concentration of 46 mg/l for 50-60 minutes. Such concentrations caused death in animals due to effects on the central nervous system or pneumonia caused by irritation of the lungs. The concentration of styrene vapors of 2 mg/l is the maximum allowable when exposed to a person for 8 hours.

Skin contact with liquid styrene should be avoided as repeated or prolonged exposure causes irritation. Taking styrene inside the body is dangerous. If it accidentally enters through the mouth, then you must immediately take an emetic, which should not contain alcohol, and call a doctor.

When storing styrene, measures should be taken to prevent spontaneous polymerization, for which some inhibitor is added to the monomer. The formation of polymer during storage is undesirable, not only because it can adversely affect subsequent work, but also because of the heat generated during this process, which becomes dangerous, especially in a closed tank, where the increase in monomer vapor pressure can create an explosion hazard.

The initiator used for polymerization, benzoyl peroxide, is an explosive substance that explodes in dry form upon impact, friction, heating, etc. Therefore, care must be taken when working with it.

Benzoyl peroxide should be stored in sealed glass or tin cans when wet (filled with water or alcohol). In dry form, benzoyl peroxide is issued only in a small amount necessary to perform the current work.

Polystyrene dust is easily electrified, when mixed with air it forms explosive mixtures, the lower explosive limit of which is 25-27.5 g/m3. Polystyrene is physiologically harmless.

Laboratory work № 2

Polymerization of methyl methacrylate at different initiator concentrations

Theoretical part

Polymerization in a block (mass) is carried out in the absence of a solvent, due to which there is no contamination of the polymer with impurities in the solvent.

To carry out such a polymerization, the solution of the initiator in the monomer is kept for the necessary time in the mold at a strictly defined temperature. If necessary, regulators and plasticizers are also added to the reaction mass. The finished polymer may be in the form of a block, rod, tube, etc. In this way, the most transparent materials are obtained, which are widely used as organic glass. Due to the increase in viscosity and decrease in the thermal conductivity of the reaction mass, the heat of reaction is not removed quickly enough. As a result, local overheating occurs, leading to the destruction of the polymer and a decrease in the degree of polymerization.

In this regard, the polymerization of different monomer layers occurs at different temperatures. The linear structure of macromolecules is disturbed and polydispersity in molecular weights increases. In addition, the monomer vapor pressure in the depth of the block, caused by overheating, creates internal stresses in the polymer. At best, such stresses lead to inhomogeneity of the block in terms of physical and chemical properties, at worst, to swelling and cracks. The larger the size of the cast sample, the more difficult it is to obtain a technically suitable material.

Significant shrinkage during block polymerization, due to the higher density of the polymer compared to the density of the monomer, reduces the accuracy of the casting. These disadvantages can be partially eliminated by polymerization at a low rate or at temperatures above the melting point of the polymer. However, this is possible if the melting of the polymer is not accompanied by its decomposition.

Esters of acrylic and methacrylic acids readily polymerize when heated in the presence of benzoyl peroxide or other radical type initiators. The polymerization of methyl methacrylate in molds finds technical application. It is possible to pour into molds both a monomer mixed with an initiator, a plasticizer, a dye or a pigment, and a syrup, which is a solution of polymethyl methacrylate in methyl methacrylate. The amount of initiator is usually in the range of 0.02-1.0% by weight of the monomer. The polymerization temperature rises gradually from 60 to 120°C. The duration of heating depends on the thickness and shape of the product (sheet, pipe, rod, etc.), the type of initiator and the purity of the monomer.

Practical part

Tasks:

1. Write the equations of chemical reactions that occur during the polymerization of methyl methacrylate in bulk

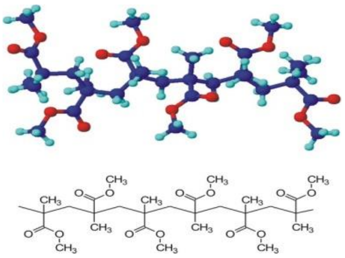
2. To carry out the synthesis of polymethyl methacrylate in bulk (block) with different content of the initiator in the reaction mixture

3. Plot the dependence of the polymerization time of methyl methacrylate on the concentration of the initiator

4. Check the physical and chemical properties of polymethyl methacrylate (relation to heating, the action of solvents, acids and alkalis, thermal insulation properties; combustion behavior)

5. Carry out the depolymerization of polymethyl methacrylate

1 stage of work. Synthesis of polymethyl methacrylate.



Reagents:

Methyl methacrylate (freshly distilled)

benzoyl peroxide

Concentrated sulfuric acid: (density 1.84 g/cm3)

Concentrated nitric acid (density 1.4 g/cm3)

Sodium hydroxide solution (10%)

Devices:

Air cooler-5 pcs

Water thermostat or bath

Chemical test tubes - 10 pcs

Supports laboratory - 2-3 pieces

Electric stove - 1 pc.

Tweezers

Scalpel

Gas-burner

glass rod

Conducting an experiment

- Take 5 tubes.
- Place 4 ml of freshly distilled methyl methacrylate and various amounts of benzoyl peroxide into each of them: #1 - 20 mg, #2 - 40 mg, #3 - 60 mg, #4 - 100 mg, #5 - 200 mg.
- Close the tubes with reflux condensers.
- Then install them on a tripod and place them in a water thermostat, on which the temperature is set to 90-95°C. The thermostat housing is made of transparent material in order to better observe the reaction.
- As a result of the reaction, a solid vitreous mass with bubbles is obtained. The reason for the formation of bubbles is that the heat released during polymerization speeds up the process. In this case, part of the monomer passes into the vapor state. Due to the high viscosity of the polymerizing mass, monomer vapors do not float to the surface, but remain inside the polymer. When the process is carried out at a lower temperature, for example, at 50-60°C, this does not happen.
- Note on the protocol the time of the polymerization reaction of MMA for each concentration of initiator.
- Plot polymerization time versus initiator concentration. Draw appropriate conclusions.
- Use the obtained polymer for the following experiments.

copolymerization reaction

Laboratory work№3

Copolymerization of styrene with methacrylic acid and analysis of copolymer composition

Reagents.

Styrene distilled - 0.1 mol (11.5 cm3, density 0.909 g/cm)

Distilled methacrylic acid - 0.05 mol (4.2 cm3, density 1.015 cm / g)

Azobisisobutyric acid dinitrile) - 0.0735 g

Dioxane or dimethylformamide - 50 cm3

Petroleum ether - 100 cm3

Potassium hydroxide solution alcohol, 0.1 N.

Phenolphthalein alcohol solution (indicator)

Devices and equipment.

Test tubes with ground stoppers 15-20 cm (2 pcs.); thermostat at 700C or a glycerin bath with a contact thermometer and a thermal relay; bottle of 50 cm3; chemical glasses for 100 cm (2 pcs.); Petri dishes (2 pcs.); conical flasks 100 or 250 cm; funnel (1 pc.); glass rods (2 pcs.); analytical balances; spatula, watch glass; pipettes 20 cm3; measuring cylinders; burettes 25 cm3

The order of the work.

On an analytical balance in a weighing bottle, the initiator is weighed in an amount of 5% of the sum of the masses of the monomers (0.0735 g). Then, styrene (0.1 mol) and methacrylic acid (0.05 mol) are added to the initiator in the molar ratio ST : MAC = 2 : 1. The bottle is closed and the contents are shaken until the initiator is completely dissolved in the monomer mixture.

After dissolution of the initiator and thorough mixing of the mixture, the contents of the bottle are poured equally into two test tubes. The tubes are closed with stoppers and placed in a glycerin bath heated to 60 - 700C.

The copolymerization of monomers is carried out until a syrupy state of the reaction mixture is reached in test tubes, and the time taken for copolymerization is measured. The tubes are removed from the bath and opened. The contents of the test tubes, while stirring with glass rods, are slowly poured into glasses with a precipitant, in which the resulting copolymer is released in the form of a viscous, thickening and hardening mass. Petroleum ether is used as a precipitant. The polymer precipitate is separated from the liquid by decantation and again thoroughly washed with a pure precipitant. Then the precipitate is unloaded onto a pre-weighed Petri dish and dried by blotting it with filter paper. Weigh and determine the total yield of the copolymer.

A sample is taken from the dried copolymer to determine its composition. The content of methacrylic acid and styrene units in the copolymer is found by the number of carboxyl groups identified in the copolymer.

Determination of the content of carboxyl groups in the copolymer

The definition is based on the interaction of carboxyl groups of methacrylic acid units with alkali:

~COOH +KOH= ~COOK +H2O

Conical flasks for titration are preliminarily weighed on an analytical balance with an accuracy of ± 0.0002 g. Samples of the investigated copolymer weighing ~0.1 – 0.2 g are taken into these flasks and weighed on an analytical balance. sew the contents until complete dissolution of the copolymer. Dioxane or dimethylformamide is used as a solvent for the copolymer. To avoid precipitation during titration, the alkali should be in the form of an alcoholic solution.

Then a few drops of phenolphthalein are added to the flasks and the contents are titrated with 0.1 N alcohol solution of KOH until a pink color appears. At the same time, a control experiment (without a sample) was set up to determine the background content of acid groups in the used solvent.

where the volumes of 0.1 n KOH solution used for titration of the sample with a weighed portion of the copolymer and the control sample, cm3;

K - correction factor of 0.1 N alcohol solution of KOH;

0.0045 - the number of ~COOH-groups corresponding to 1 cm of exactly 0.1 n KOH solution, g/cm;

According to the amount of alkali used for titration, the content of carboxyl groups [COOH] in mass% in the studied copolymer is determined according to the following formula:

m is the weight of the copolymer taken for titration, g.

For the final result, take the arithmetic mean of the analysis of two samples.

Processing of results.

The content of methacrylic acid units in the copolymer [MAA mass] in % (mass) is determined by recalculation from the found content of carboxyl groups according to the formula

where MMAC is the mass of the methacrylic acid unit, g/mol;

MOOH is the mass of the carboxyl group COOH, g/mol;

[COOH] - the content of carboxyl groups found above in the copolymer, %.

The content of styrene units in the copolymer [STmass] in % (mass) will be equal to:

[STmass] = 100 - [MACmass].

[STM(I] = 1 - [MAK Mol].

According to the content of units of styrene [STmol] and methacrylic acid [MACMol], expressed in mole fractions, find the molar ratio of these monomers in the copolymer: [STmol] : [MACMol].

The resulting ratio is compared with the molar ratio of monomers in the initial mixture and conclusions are drawn about the activity of the monomers in the copolymerization reaction.

Dividing the mole fraction of the corresponding monomer in the copolymer

for the time t from the start of the copolymerization process to the moment of syrup formation (thickening of the mixture), the copolymerization rate is calculated for each of the monomers.

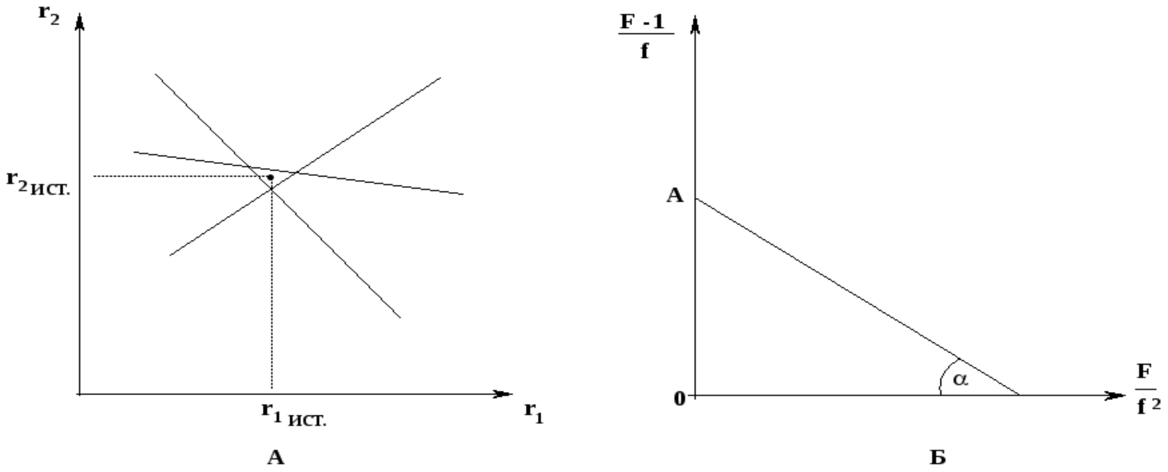
Report requirements.

1. Prepare a draft report in advance, highlighting in it the answers to the tasks indicated in the Introduction.
2. Give a brief method of work, recipe and required calculations.
3. Describe the chemistry of the stages of radical copolymerization of styrene and methacrylic acid.
4. Reflect the main properties and applications of styrene copolymers.
5. Draw a copolymerization plant.

6. Compare the ratio of monomers in the initial mixture with the ratio of units in the copolymer and draw conclusions about the activity of the monomers involved in copolymerization. Compare the obtained results with the literature data on the values of the copolymerization constants of styrene and methacrylic acid.

Determination of the copolymerization constant

To experimentally determine the copolymerization constants of two monomers, several mixtures of these monomers are prepared with different ratios, from a noticeable excess of one to a noticeable excess of the other. Each mixture is subjected to copolymerization to small depths of monomer conversion (recall that at any greater depths, the quasi-stationarity condition does not apply, and the Mayo-Lewis equation loses its force). Of course, all mixtures are copolymerized under the same conditions. Each copolymer is isolated from the reaction mixture (for example, by precipitation) and its composition is determined by chemical or physical methods. This composition is conditionally considered differential (d[A]/d[B]); this is not quite correct, but does not distort the results too much. The results obtained are processed; There are two processing options:



1. Mayo-Lewis method. For each mixture of monomers, the corresponding values [A]/[B] (given) and d[A]/d[B]) (found) are substituted into the Mayo-Lewis equation; we obtain a linear equation with two unknowns - r1 and r2. Based on this equation, they build a graph of the dependence of one constant on another; it is a straight line. If the experiment is carried out correctly, the lines for different mixtures of monomers intersect in a fairly limited area (Fig. 4, A):

Rice. 4. Calculation of experimentally determined copolymerization constants

A. According to Mayo-Lewis; B. According to Feynman - Ross

The coordinates of the center of this region of intersection of lines (r1 source and r2 source) correspond to the values of the constants r1 and r2 for a given pair of monomers under given conditions.

$$\frac{\mathbf{F - 1}}{\mathbf{f}} = \mathbf{r_1} - \frac{\mathbf{F}}{\mathbf{f^2}} \cdot \mathbf{r_2}$$

2. The Feynman-Ross method. Denoting d[A]/d[B] as F and [A]/[B] as f, and after a series of transformations, the Mayo-Lewis equation is brought to the form:

Using the values of [A] and [B] and the found values of d[A] and d[B], calculate the values of F and f for each mixture of monomers, and then build a graph in the coordinates F/f2 - (F-1)/f ; it is a straight line (Fig. 4b). This straight line cuts off the value r1 on the y-axis (segment 0A); the tangent of the slope of the straight line to the x-axis (tg□) gives the value of r2.

Theoretical calculation of copolymerization constants

As already mentioned, the copolymerization constants characterize the comparative reactivity of the monomers and the radicals formed in the reaction, i.e. they are directly related to their structure. This makes it possible in principle to calculate the copolymerization constants a priori.

So far, it has not been possible to find exact quantitative patterns relating the values of the copolymerization constants to the structure of the particles involved in the process. However, it was possible to find some correlation dependences, which, to some extent empirically, make it possible to predict the values of the copolymerization constants (of course, only with a certain degree of approximation). Among these correlation dependences, the most well-known is the so-called Q-e scheme of Alfrey-Price (Alfrey-Price, 1947).

According to this scheme, the affinity of the polymer radical and the monomer (which determines the easiness of any elementary chain propagation reaction) is determined by the following factors:); 2) factor Q - a value characterizing the activity of the monomer (for monomer A - Q1, for monomer B - Q2); 3) the factor e is a value that characterizes the polarity of the monomer and the corresponding radical (for A and ~A▪ - e1, for B and ~B▪ - e2). For simplicity, it is assumed that the polarity factor for the monomer and the corresponding radical is the same. This, in fact, is not quite correct, but it does not noticeably worsen the correlation. At the same time, for electron-rich monomers (for example, vinyl monomers containing a donor substituent X at C=C bonds, such as butylvinyl ether CH2=CH-OBu), the value of the factor e is taken as negative, and for electron-deficient ones (for example, acrylonitrile CH2=CH→CN) - positive.

According to Alfrey-Price, the rate constants of elementary chain propagation reactions in radical copolymerization are related to these factors as follows:

$$k_{11} = P_1Q_1\exp(-e_1^{2}) \qquad k_{22} = P_2Q_2\exp(-e_2^{2})$$

$$k_{12} = P_1Q_2\exp(-e_1e_2) \qquad k_{21} = P_2Q_1\exp(-e_2e_1)$$

Следовательно, для констант сополимеризации:

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2}\exp[-e_1(e_1 - e_2)]$$

$$r_2 = \frac{k_{22}}{k_{21}} = \frac{Q_2}{Q_1}\exp[-e_2(e_2 - e_1)]$$

Thus, to calculate the copolymerization constants, it is necessary to know the values of the factors Q and e. In this case, it is not the absolute values of these factors that are important here, but their ratio for different monomers (the above equations are correlation equations). Therefore, here, as a “starting point”, one can choose a certain “reference” monomer, assign to it some, in general, arbitrary values of the factors Q and e (however, on condition that the order and sign of these factors are somehow consistent with the structure of the monomer) , and then experimentally compare other monomers with the reference one.

Styrene was chosen as the reference monomer (perhaps the most "universal" monomer); the values were assigned to it: Q = 1, e = - 0.8. To determine the values of the Q and e factors for any monomer, it is copolymerized with styrene and the copolymerization constants r1 and r2 are experimentally determined. The found values of the constants are substituted into the above equations and two equations are obtained with two unknowns Q2 and e2 (because Q1 = 1, e1 = - 0.8); the solution of the equation gives the desired values.

In this way, the values of the Q and e factors were experimentally determined for many monomers; by choosing any pair of these monomers, one can calculate the copolymerization constants for this pair (for the same conditions under which the values of Q and e were determined. The reliability of these calculations is far from 100%, but still allows one to predict the order of magnitude of the copolymerization constants and their ratio, and in many cases, assign a pair of monomers to one of the four groups mentioned above.

An analysis of the Alfrey-Price equations above shows that if the polarity of the monomers is opposite (the factors e have different signs), then both copolymerization constants will be less than unity, i.e. the copolymer will tend to alternate. Therefore, if, for example, the task is to obtain a partially alternating copolymer of two vinyl monomers, you need to choose a pair where one monomer contains a donor substituent in the C=C bond, and the other is an acceptor substituent. There is an assumption that such a "donor-acceptor" pair of monomers forms a charge-transfer complex, which increases the rate of copolymerization and further promotes alternation.

The study of copolymerization, in addition to its obvious applied interest, is also of very important theoretical significance, since it makes it possible to obtain important information about the reactivity of monomers.

The patterns of copolymerization of three monomers are in principle similar to those described above, but the calculations here are more cumbersome (for example, it is necessary to take into account not two, but six copolymerization constants).

The regularities of radical copolymerization considered here are in many respects applicable to ionic copolymerization as well. The formation of a copolymer chain, as in radical processes, proceeds at the stage of growth according to the chain mechanism, through the interaction of the active center with the monomer.

Polycondensation reaction

Laboratory work №4

Polycondensation of citric acid and ethylene glycol

Reagents:

Citric acid - 1 mol
Ethylene glycol - 1.3 mol
A mixture of ethanol: benzene (1: 1) - 100 ml
Potassium hydroxide, KOH, 0.1 M alcohol solution - 100 ml
Phenolphthalein, 1% alcohol solution Acetone

Devices:

Round-bottom three-necked flask with a capacity of 100 ml - 1 pc.
Dean-Stark nozzle, 10 ml - 1 pc.
Thermometer (with a thin section) - 1 pc.
Reverse ball cooler - 1 pc.
Mantle heater - 1 pc.
Conical flasks with a capacity of 50 (100) ml for titration - 5 pcs.
Glass tube for sampling - 5 pcs.
Graduated cylinder, 20 (25) ml – 1 pc.
Burette for titration, 10 (25) ml – 1 piece
Glass glass, 100 ml - 2 pcs
Mechanical stirrer with motor - 1 pc.
Crucible, Porcelain Cup
Laboratory tripod - 2 pcs

glass rod

Soxhlet apparatus

Muffle Furnace (180°C)

Conducting an experiment

Citric acid and ethylene glycol are loaded into the reaction flask of the device. The contents of the flask are gradually, over 25-30 minutes, with stirring, heated on a mantle heater to 150-155°C. Polycondensation is carried out at this temperature until a product is obtained, which forms a brittle glassy mass when the sample is cooled.

To determine the kinetics of the polycondensation process, after 10, 20, 30, 60, 90 minutes after obtaining a homogeneous mixture, samples of 0.3-0.4 g are taken into pre-weighed conical titration flasks with an accuracy of 0.0002 g, in which the acid number is determined . Simultaneously with sampling, note the amount of water released in the Dean-Stark nozzle. According to the obtained values of the acid number and the amount (mass) of the released water, graphical dependences of these indicators on the time of polycondensation are built.

At the end of the polycondensation, the heated resin is poured from the flask into a pre-weighed porcelain cup. After cooling, the cup of resin is weighed. In one part of the resin, the melting point is determined. Another part of the resin is placed in a crucible, which is kept in a muffle furnace at 200°C for 15 minutes. Then, the content of sol and gel fractions in the cured product is determined by extracting a sample of the resin with acetone in a Soxhlet apparatus.

The results are presented in the form of tables.

Table 1

Loading						**Yield of mass**	
Ethylene glycol			**Citric acid**		**Total mass**		
mol	**gr**	**ml**	**mol**	**gr**	**gr**	**gr**	**mas.% from theoret.**

Table

Time from the beginning of the experiment,min	**Resin weight, gr**	**Amount of 0,1M KOH, ml**	**Acid number (AN), mg KOH/gr**	**Amount of released water, ml**
0				
10				
20				
30				
60				
90				

Laboratory work № 5.
Polycondensation of phenol with formaldehyde

Reagents: phenol - 9.4 g; formalin - 4 ml (4 g); HCl - 0.1 ml.

Equipment: three-necked flask, reflux condenser, thermometer, porcelain cup, water bath, tin sheet.

A mixture of phenol and formalin is shaken in a 100 ml round-bottom flask until complete dissolution, then 0.1 ml of hydrochloric acid is added, a reflux condenser is attached to the flask and heated in a water bath at 90-100°C for 20-40 minutes. The reaction proceeds with the release of heat. When the mixture boils, the heating is stopped. Then heating is continued in a boiling water bath until the reaction mass is divided into two layers: the upper layer is aqueous (usually cloudy) and the lower one is thick, light yellow or light brown (depending on the quality of phenol), which is a polycondensation product.

1. The contents of the flask are poured into a porcelain cup. After cooling, the top layer is separated. The polymer product remaining in the cup is washed

with warm water until neutral with methyl orange and dried, gradually heating to 200°C.

Chemical properties of polymers

Laboratory work №6

Partial hydrolysis of polyacrylonitrile fiber (Nitron)

The colorimetric method for determining residual polyacrylamide in water is based on the hydrolysis of polyacrylamide with alkali and the determination of ammonia nitrogen using Nessler reagents. When analyzing ammoniacal polyacrylamide, the ammonia introduced with ammonium sulfate must first be removed. Removal of ammonia is achieved by distillation with a buffer solution at pH = 7.4 or by passing the solution through a column.

Polyacrylamide (PAA) is usually obtained by radical polymerization in the presence of redox initiating systems at temperatures not exceeding 50 °C. At higher temperatures, highly branched or cross-linked polymers are formed, and hydrolysis of polyacrylamide can also occur. Polymerization is carried out mainly in aqueous solutions, which are then used for their intended purpose. If necessary, PAA is isolated from the solution by evaporation under vacuum. The heterogeneous polymerization of acrylamide can also be used to obtain PAA.

Operation procedure 1) carrying out alkaline hydrolysis of polyacrylamide and acrylamide in aqueous solutions 2) determination of the degree of polymer and monomer hydrolysis in samples of the reaction mixture.

The essence of the method. The method is based on alkaline hydrolysis of polyacrylamide, which leads to the replacement of amide groups in it by hydroxyl groups, adsorption of the formed polyacid by calcium carbonate from an acidic medium, then formation of a dark blue product of addition of methylene blue to this polyacid on the surface of calcium carbonate, elution of the resulting colored compound with water and measurement optical density of an aqueous solution. The effect of neighboring units is the influence of the reacted functional groups in the macromolecule on the reactivity of neighboring groups. As a result, the reactivity of the functional groups may change with the degree of conversion. An example of such a reaction is the alkaline hydrolysis of polyacrylamide. The rate of hydrolysis of polyacrylamide is higher than that of acrylamide, which is explained by the promotion of hydrolysis of the amide groups of the nearest ionized carboxyl groups (I). However, at deep conversions, blocking of amide groups by two ionized carboxyl groups (II) can occur, which leads to incomplete alkaline hydrolysis of polyacrylamide (under normal conditions, the degree of conversion does not exceed 70%) and slows down the reaction rate.

Laboratory work №7

Alcoholysis of polyvinyl acetate (alkaline method)

Reagents.

A solution of polyvinyl acetate (PVA) in ethyl alcohol (30%) - 30 g;

A solution of alkali in ethyl alcohol

(11.25 g KOH or 9 g NOH in 100 cm3 of alcohol - 60 cm3;

Phenolphthalein alcohol solution (indicator)

Devices and equipment.

250 ml or 500 ml three-necked flask equipped with a stirrer

hermetic seal; dropping funnel with a volume of 150-200 cm; laboratory transformer; measuring cylinder with a capacity of 100 cm; Bunsen flask with Buchner funnel; technical and analytical scales; drying cabinet; Petri dishes, water jet or vacuum pump.

The order of the work.

In a three-necked flask with a capacity of 250 (500) cm3, equipped with a stirrer with a hermetic closure and a dropping funnel, pour 60 cm3 of an alcohol solution of alkali. 30 g of a 30% alcohol solution of polyvinyl acetate (PVA) is placed in a dropping funnel. Turn on the stirrer and add polyvinyl acetate dropwise to the alkali solution at room temperature. Adjust the rate of dropping the PVA solution at the level of 4-5 drops per minute.

In the course of the reaction of hydrolysis of the side acetate groups of the PVA molecules, the initial colorless PVA solution turns into a yellowish-brown polyvinyl alcohol precipitate in the flask. The duration of the reaction is 2-3 hours.

At the end of the hydrolysis process, the precipitate of polyvinyl alcohol (PVA) is filtered off on a Buchner funnel, washed several times with acetone until the indicator is neutral, and dried to constant weight on a pre-weighed Petri dish in an oven or in air at room temperature for a week. The dried polyvinyl alcohol (PVA) is weighed and the yield of the product is determined.

The degree of conversion of acetate groups into alcohol ones is judged by the yield of the product.

Report requirements.

1. Prepare a draft report in advance, giving answers to the points indicated in the Introduction.
2. Draw a diagram of the installation.
3. Give the chemistry of the reaction of alkaline hydrolysis of polyvinyl acetate and the calculation of the theoretical yield of PVA.
4. Specify the properties and applications of polyvinyl alcohol.
5. Perform the required calculations, determine the product yield and draw conclusions based on the results of the work.

VI semester

Laboratory work № 8

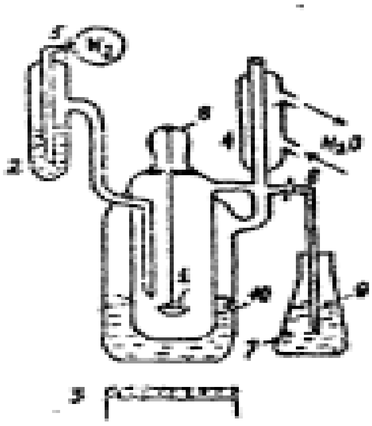
Thermic destruction of polyvinyl chloride

The purpose of the work: to investigate the thermal degradation of polyvinyl chloride (or perchlorovinyl) in an inert gas atmosphere.

Reagents: 0.05 N a solution of polyvinyl chloride (or perchlorovinyl), NaOH and HCl.

Equipment: equipment for thermal destruction of a PVC electric stove, a nitrogen cylinder, 6 conical flasks of 250 ml each.

Performance of work: 1) thermal destruction of polyvinyl chloride (perchlorovinyl) in an inert gas environment; 2) determine the degree of destruction with hydrochloric acid obtained from the destruction.



equipment used for thermal destruction the tightness of the equipment shown in the picture is checked. For this purpose (2), nitrogen is injected through the dryer from a gas cylinder at a constant rate of 1 bubble per second. Observe the evolution of gas through a 250 ml conical flask (7) containing 15 ml of distilled water. When sufficient tightness is achieved, the gas flow in tanks (2) and (7) equalizes and the valve (5) closes. The electric stove (3) and the refrigerator (4) are connected to water, and the water (10) is heated to boiling. In 5 conical flasks with a capacity of 250 ml, pour 15 ml of 0.05 N. NaOH solution, lower the test tube into the flask 9), 8) take a cap cap, place (0.12-0.20 g) a sample of polyvinyl chloride (perchlorovinyl) in a glass (1), hang it on a special suspension and lower it into the flask. Level - slowness (6) open the shut-off valve. The throughput of passing gaseous hydrogen chloride should be 1 bubble per second. Gas absorption is carried out for 10, 15, 20, 25 and 30 minutes, and the excess NaOH solution in each flask is supplemented with hydrogen chloride and titrated with a 0.05 N solution, the results are recorded in the following table.

№	**Volume 0.05 N NaOH (mL)**	**Gas absorption time (minutes)**	**Volume of HCl used for titration (ml)**	**The amount of HCl released since the beginning of the reaction (ml)**
0	15			
1	15			

2	15			
3	15			
4	15			

Laboratory work №9

Hydrolytic degradation of polyamide

Purpose: to study the kinetics of hydrolytic degradation of polyamides by gravimetric method in sulfuric acid solution.

Reagents: polyamide grains (kapron, nylon); 15, 20, 25 and 30% solutions of sulfuric acid, distilled water.

Equipment: hydrolysis equipment, reverse cooler, electric stove.

Performance of work: gravimetric transfer of the kinetics of hydrolytic degradation of capron (nylon) in sulfuric acid solutions.

1. Check the integrity of the device and the presence of water in the refrigerator.

2. Weigh 0.1 g of nylon grains on an analytical balance and place them in a special cup (2).

3. Pour the sulfuric acid solution into the flask (2) until the sample is immersed in water, place the polymer beaker (1) in the instrument and quickly heat on the electric stove (3) until the acid solution boils.

4. During the reaction, take the polymer beaker (1) every 10 minutes, extrude the sample into filter paper and weigh the sample on an analytical balance. in total, the measurement is repeated 6 to 8 times.

Laboratory work №10

Influence of the Nature of the Solvent on the Swelling Rate of Crosslinked Polymers

Objective: To measure the swelling rate and swelling ratio of vulcanized sodium butadiene rubber (rubber) in toluene and ethyl acetate. Reagents: SR-2 rubber, toluene, ethyl acetate.

Equipment: (2 pcs.), Stopwatch, rubber bulb, analytical scales.

Performance of work: The swelling rate is measured by the volumetric method on a nabuxometer. 2 pieces of rubber weighing about 0.1-0.2 g are weighed on an analytical balance, pre-calibrated, nabuxometers, one filled with toluene and the other with ethyl acetate. The swelling of the rubber is observed by measuring the amount of liquid absorbed every 10 minutes for 3 hours in parallel in both solvents.

Systems:

t - time in minutes from the beginning of the experiment; h is the height of the liquid in the nabuxometer tube (the amount of liquid corresponding to the divisions in the graduated tube is indicated on the nabuxometer); V1-volume of swallowed liquid, ml; m0 - initial mass of rubber, g; q∞ is the maximum degree of swelling, r is the density of the liquid.

Results

T	**h**	**V_1**	**$q = V_1 * \rho / m_0$**	**$\lg(q_\infty - q)$**

Based on the results obtained, graphs of the degree of swelling q and lg (q∞-q) versus time were plotted for both solvents. The bending constants of rubber in toluene and ethyl acetate are found by the equation:

$\lg (q_\infty - q) = \lg q_\infty - k.t$

Returns the value of the tangential angle (bending constant) of the deflection of a straight line in a lg (q∞-q) versus time plot.

Task: Explain that the rate of swelling of rubber in both solvents will be different.

Laboratory work №11

Determination of molecular weight by viscometric method

Purpose: to calculate the molecular weight by determining the viscosity of polymer solutions of different concentrations.

Equipments: thermostat, modified Ubbelohde viscometer, stopwatch, pipette (10 ml), rubber tube, rubber bulb, polyacrylamide, polyvinylpyrrolidone, polystyrene, polymethyl methacrylate, or other polymers (provided by the teacher). Concentrated solutions 0.2-0/100 ml.

Performance of work: Polymer, solvent and temperature for work are selected according to this table. This table also shows the K and α values of the Mark-Kuhn-Houwink equation for experimental conditions.

First, the solvent is poured into a clean, dried viscometer and, using a rubber bulb, rises to the top of the viscometer container with 2 tubes closed. When the neck of the tube 2 opens, the solvent begins to flow from the cylinder to the bottom of the viscometer. The flow time from the mark on the top of the balloon to the top of the capillary is measured 3-4 times with a stopwatch. The first solution is then poured into a clean, dried viscometer. The volume of the solution (usually 7-8 ml) should be sufficient to fill the capillaries, upper and lower vials of the viscometer. The polymer solution must be accurately measured with a pipette.

The transition period of the first poured solution through the vial of the viscometer is measured in the same way as with the solvent. Dilution of polymer solutions is carried out on the same viscometer. To do this, pour an equal volume of solvent onto the initially obtained solution, wait 15-20 minutes until the solution is balanced and its temperature reaches the temperature of the thermostat. Dilution of the solution is carried out at least 3 times. the work to be done at each concentration of the solution is done as described above. That is, in order to determine the flow time of other concentration solutions, a certain amount of solvent is added to the solution in the viscometer using a pipette, and the flow time of the solution concentration is measured accordingly.

The concentration of dilute solutions is calculated using the following equation:

$$C_2 = \frac{C_1 + V_1}{V_1 + V_2}$$

- concentration of the solution in the viscometer, g / dl.

- concentration after adding a certain amount of solvent to the solution, g / dL.

- - the amount of solution in the viscometer, ml.

- amount of added solvent, ml.

The results are listed in the following table:

Flowing time of solvent. t_0**, sec**	**Flowing time of solution.** t_0**, sec**				
	$V_1 = 5\ мл$	$V_2 = V_1 + 1\ мл$	$V_3 = V_2 + 2\ мл$	$V_4 = V_3 + 3\ мл$	$V_5 = V_4 + 5\ мл$
1. 2. 3. 4. 5.					
average					

The results of the intrinsic viscosity calculation are entered in the following table:

t₀- Pure solvent flow time, sec.

№	**Solution concentration, C,%**	**Flowing time of solution, t_1, sec**	$\eta_{нис} = \frac{t_1}{t_0}$	$\eta_{сол} = \frac{t_1}{t_0} - 1$	$\eta_{кел} = \frac{\eta_{сол}}{c}$	$\ln\left(\frac{\eta_{nis}}{C}\right)$

Laboratory work №12

Determination of the isoelectric point of polyampholyte

Purpose: to determine the isoelectric point of gelatin by viscometry.

Equipment: pH meter, analytical balance, viscometer, stopwatch, rubber bulb, 50 ml beaker, 50 ml flat test tube, 25 ml cylinder, 2 x 20 ml burets; gelatin, 0.02 N NaOH. solution in water 0.03 N. HCl. solution in water.

Execution of work. The isoelectric point of gelatin is determined by the change in the viscosity of its solution during titration with alkali and acid. Gelatin is prepared from 50 ml of a 1% solution in water. the solution should be constantly stirred, the temperature should not exceed 40oC.

Take 20 ml of the prepared solution and add 0.03 N. Titrate with HCl solution while measuring the viscosity of the solution. Viscosity is 4.75 pH at initial dilution and titration; 4.5; 4.25; 4.0; 3.5; Approximately 2.5 and 2.1. At the end of the titration, the electrodes of the pH meter are washed with distilled water, and the viscometer with hot water, and the time of distilled water outflow is determined.

Similarly, in 20 ml of fresh gelatin solution 0.02 N. Titrate with NaOH. The viscosity is 6.0 pH of the stock solution; 7.0; 8.0; It is measured in aisles 9.0 and 10.0.

The results obtained are presented in the table below.

to - solvent (pure water) outflow time up to s

Added amount of alkali or acid, ml	**pH**	**t-solution outflow time, sec.**	$\eta_{rel} = t/t_o$	$\eta_{сол} = t/t_o - 1$

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ЎЗБЕКИСТОН РЕСПУБЛИКАСИ
ОЛИЙ ВА ЎРТА МАХСУС ТАЪЛИМ ВАЗИРЛИГИ

ЎЗБЕКИСТОН МИЛЛИЙ УНИВЕРСИТЕТИ

"ТАСДИҚЛАЙМАН"
ЎзМУ ректори
2020 йил 30 июнь

"КЕЛИШИЛДИ"
Олий ва ўрта махсус таълим вазирлиги
2020 йил 29 август

Рўйхатга олинди: № БД-5140500-2.09
2020 йил 29 август

ЮҚОРИ МОЛЕКУЛЯР БИРИКМАЛАР КИМЁСИ

ФАН ДАСТУРИ

Билим соҳаси:	100000	– Гуманитар соҳа
Таълим соҳаси:	140000	– Табиий фанлар
Таълим йўналиши:	5140500	– Кимё (турлар бўйича)

ТОШКЕНТ – 2020

Фан/модуль коди YMBB310	**Ўқув йили** 2022-2023	**Семестр** 5-6	**ECTS - Кредитлар** 10	
Фан/модуль тури Мажбурий	**Таълим тили** Ўзбек/рус		**Хафталаги дарс соатлари** 4	
1.	**Фаннинг номи**	**Аудитория машғулотлари (соат)**	**Мустакил таълим (соат)**	**Жами юклама (соат)**
	Юкори молекуляр бирикмалар кимёси	120	180	300

2.

I. Фаннинг мазмуни

Фанни ўкитишдан максад - талабаларга полимерлар молекулаларининг катта ўлчами ва занжирсимон тузилишга эгалиги сабабли, оддий куйимолекуляр моддалардан фаркланувчи ўзига хос хоссаларини тушунтиришдан ва бу хоссалардан фойдаланишда амалий кўрсатмалар беришдан иборатдир. Полимер моддалар макромолекуласининг хусусиятлари, полимерларнинг синтези ва унинг мухим конуниятлари, физик-кимёвий ва физикавий-механик хоссаларининг асосий хусусиятлари, полимерлар кимёсида кўлланадиган усуллар ва саноатда хамда турмушда кенг кўлланиладиган полимерлар хакида йўналиш профилига мос кўникма ва малака шакллантиришдир.

Фаннинг вазифаси - полимерларнинг куйи молекуляр бирикмалардан фаркини; полимерларнинг ўзига хос хусусиятларини; талабаларда полимерларнинг синтези, физик кимёвий хоссаларни; полимерлар эритмаларининг хоссаларини тахлил ва тадкик этишни; янги турдаги полимерларнинг яратиш илмий асосларини тузилиш ва хосса муносабати конуниятлари оркали ўргатиш; янги шаклланаётган ва оммалашаётган фан ва технологияларни тараккий эттиришда юкори молекуляр бирикмалар ўрнини кўрсатишдан иборат.

II. Асосий назарий кисм (маъруза машғулотлари)

II.I. Фан таркибига куйидаги мавзулар киради:

1- мавзу. Юкори молекляр бирикмалар хакида асосий тушунчалар

Юкоримолекуляр бирикмалар, олигомер, полимерлар. Макромолекула ва унинг кимёвий звеноси. Полимерланиш даражаси ва занжир узунлиги. Полимерларнинг тирик табиатдаги роли ва уларнинг кимёвий материаллар сифатида ахамияти. Полимерлар хакидаги фаннинг ривожланиш тарихи. Полимерлар кимёси фанини ривожлантиришда Ўзбекистон олимларининг хизматлари.

2- мавзу. Полимерларнинг синфланиши

Полимерларнинг келиб чикиши, кимёвий таркиби, звенолари ва асосий занжир тузилишига караб синфлаш. Табиий, сунъий ва синтетик полимерлар. Органик ва анорганик полимерлар Чизикли, тармокланган ва чокланган полимерлар. Гомополимерлар, сополимерлар, блок-сополимерлар ва пайвандли сополимерлар. Гомозанжирли ва гетерозанжирли полимерлар.

3- мавзу. Полимерларнинг кимёвий синфланиши.

Моноолефинлар ва улар ҳосилаларининг полимерлари ва сополимерлари. Полиэфирлар. Полиацеталлар. Полиамидлар, полиуретанлар. Полисилоксанлар.

4- мавзу. Полимерларнинг молекуляр массаси хақида тушунча

Полимерларнинг молекуляр массаси, молекуляр-массавий тақсимланиши ва ўртача молекуляр масса тушунчаси. Ўртача рақамли ва вазний молекуляр массалар. Полидисперслик даражаси.

5- мавзу. Полимерлар синтези. Радикал полимерланиш

Полимерларни синтез қилишнинг асосий усуллари. Занжирли ва босқичли полимерланиш. Радикал полимерланиш. Радикал полимерланишни иницирлаш. Фотокимёвий полимерланиш. Инициаторлар. Радиацион полимерланиш. Термик полимерланиш. Радикал полимерланиш босқичлари. Ривожланиш, узилиш ва занжир узатилиш реакциялари. Кинетик занжир узунлиги ва унга таъсир қилувчи омиллар. Ингибиторлар. Бошқарувчилар.

6- мавзу. Радикал полимерланиш кинетикаси

Радикал полимерланиш кинетикаси. Радикал полимерланиш кинетикасига таъсир этувчи омиллар. Радикал полимерланиш кинетикасининг умумий тенгламаси.

7- мавзу. Полимерланиш термодинамикаси

Полимерланиш жараёнидаги энтальпия ва энтропия ўзгариши. Мономер тузилишининг полимерланишга таъсири. Юқори конверсияда полимерланиш

8- мавзу. Сополимерланиш

Сополимерланиш хақида тушунча. Сополимерланиш реакцияси. Сополимерланишнинг Майо-Льюис таркиб тенгламаси. Сополимерланиш диаграммаси.

9- мавзу. Сополимерланиш константалари ёрдамидаги хисоб - китоблар

Сополимерланиш константалари ва уларни аниқлаш усуллари. Альфрей - Прайснинг Q-е схемаси. Сополимерларни таркиб бўйича кўпжинслийлиги.Сополимер занжирларининг микроструктураси.

10-мавзу. Ионли полимерланиш

Катион полимерланиш. Катализаторлар ва ҳамкор катализаторлар. Катион полимерланиш механизми Катион полимерланишдаги занжир узулиши. Катион полимерланиш кинетикаси.

11- мавзу. Анион полимерланиш

Анион полимерланиш катализаторлари. Анион полимерланиш кинетикаси ва механизми. Координацион - ионли полимерланиш. Циглер - Натта катализаторлари.

12-мавзу. Поликонденсатланиш реакцияси

Поликонденсатланиш реакцияларининг хиллари. Поликонденсатланишнинг йўналиши. Поликонденсатланиш реакциясининг кинетика ва термодинамикаси. Мувозанатли поликонденсатланиш.

13.-мавзу. Поликонденсатланишда молекуляр массага таъсир этувчи омиллар

Карозерс тенгламаси. Коршакнинг ноэквивалентлик қоидаси. Поликонденсатланишдаги деструктив реакциялар. Босқичли (миграцион) полимерланиш. Циклик бирикмаларнинг чизиқли полимерларга айланиши.

14-мавзу. Саноатда полимерларни олиш усуллари

Эритмада, блокда ва қаттиқ фазада полимерланиши. Эмульсион ва суспензион полимерланиш. Эритмада, массада ва фазалар аро мухитда поликонденсатланиш

15-мавзу. Полимерларнинг физикавий кимёси. Полимерларнинг букулувчанлиги

Конфигурацион изомерия ва макромолекулаларнинг конфигурацияси. Конформацион изомерия ва макромолекулаларнинг конформацияси. Макромолекулалардаги ички айланиш имкониятлари ва букилувчанлик. Макромолекула учлари орасидаги ўртача квадратик масофа. Статистик сегмент тушунчаси. Кун сегменти. Кинетик ва термодинамик букилувчанлик ва уларни аниқлаш усуллари.

16-мавзу. Полимерларнинг устмолекуляр структураси

Аморф ва кристалл полимерлар. Полимерлар физикавий хоссаларининг ўзига хослиги. Релаксацион ҳодиса. Полимерларнинг фазавий ҳолатлари. Полимерларнинг кристалланишига таъсир этувчи омиллар.

17-мавзу. Полимерлар физик холатлари

Аморф полимерларнинг уч физик ҳолатлари. Шишасимон, юқори эластик ва қовушқоқ - оқувчан ҳолатларнинг полимер молекуляр массасига боғлиқлиги.

18-мавзу. Полимерларнинг мустахкамлиги

Кристалл ва амор полимерларнинг механик хоссалари. Полимерлар мустахкамлиги ва эксплуатацион хоссалари. Пластификация механизми. Пластификаторларга қўйиладиган талаблар. Каргин ва Журков қоидалари. Полимерларни полимерлар билан пластификациялаш.

19-мавзу. Полимерлар эритмалари назарияси

Эритмалар назариясининг ривожланиш тарихи. Полимер эритмаларини тайёрлаш ва тозалаш. Полимерлар эрувчанлиги ва унга таъсир қилувчи омиллар. Эрувчанликнинг термодинамик мезони ва эритмалар термодинамик мувозанатининг исботи. Полимер - эритувчи системасининг фазавий диаграммаси. Полимерларни фракциялаш усуллари.

20-мавзу. Полимерларнинг эриш жараёни

Полимерларнинг бўкиши. Бўкиш даражаси. Бўкиш кинетикаси ва унга таъсир этувчи омиллар. Полимер эритмаларида ассоциланиш ва сольватланиш. Эритма компонентлари орасидаги мойиллик. Полимер эритмалари термодинамикасининг Флори - Хаггинс назарияси. Полимер эритмаларининг осмотик босими. Иккинчи вириал коэффициент ва унинг Флори - Хаггинс параметри билан боғлиқлиги. Тэта ҳолат ва тэта эритувчи тушунчалари.

21-мавзу. Полимер эритмаларининг гидродинамик хоссалари

Полимер эритмалар қовушқоқлиги. Нисбий, келтирилган ва характеристик қовушқоқлик. Характеристик қовушқоқликнинг молекуляр масса билан боғлиқлиги.

22-мавзу. Полимерларнинг молекуляр массасини аниқлаш усуллари

Седиментация ва диффузия, нур ёйиш усуллари билан полимерларнинг молекуляр массасини аниқлаш. Эритмадаги макромолекулаларнинг ўлчами ва шаклини аниқлаш усуллари.

23- мавзу. Полимер ивиқлар

Полимерларнинг концентрланган эритмалари. Концентрланган эритмалар қовушқоқлиги ва гистерезиси. Ивиқланиш ва ивиқлар.

24-мавзу. Полиэлектролитлар

Полиэлектролитлар синфланиши. Полиэлектролитлар эритмалари хоссаларининг ўзига хослиги. Полиамфолитлар. Изоэлектрик нуқта. Оқсиллар-амфотер полиэлектролитлар тимсоли. Полииэлектролитларнинг гидродинамик хоссалари

25-мавзу. Полиэлектролитлардаги ион мувозанат

Полиэлектролитларни потенциометрик титрлаш. Полиэлектролитлар учун Гендерсон-Гассельбах тенгламасининг ўзига хослиги. Интерполимер комплекслар. Полиэлектролитларнинг амалий аҳамияти. Ионалмашинувчи полимерлар.

26-мавзу. Полимерларнинг кимёвий хоссалари

Полимерлар кимёвий хоссаларининг турлари. Функционал гуруҳларнинг кимёвий хоссалари. Полимераналогик ва ички молекуляр ўзгаришлар. Уларнинг механизми ва кинетикаси. Функционал гуруҳлар реакцион қобилиятининг ўзига хослиги: локал қамал, конфигурация, макромолекулаларнинг конформацияси ва полимерлар устмолекуляр структурасининг таъсири, қўшни гуруҳ, концентрацион ва электростатик самаралар.

27-мавзу. Макромолекулалараро реакциялар

Полимерларни кимёвий модификациялаш. Каучукни вулқонлаш. Блок ва пайвандли сополимерлар олиниши ва хоссалари.

28-мавзу. Полимерларнинг деструкцияси

Полимерланиш даражасининг камайишига олиб келувчи реакциялар. Деструкция. Кимёвий агентлар таъсирида содир бўлувчи деструкция.

Физикавий деструкция. Деструкция механизмлари. Полимерларнинг эскириши. Ҳаво, нур, радиация таъсиридаги деструкциялар.

29-мавзу. Полимерларни стабиллаш

Деструкцияни тезлатувчи ва секинлатувчи моддалар. Полимерларни стабиллаш усуллари. Стабилизаторлар ва уларга қўйиладиган талаблар.

30-мавзу. Кичик тоннажли полимер материаллар

Полимер композицион материаллар, махсус хоссали полимер материаллар хақидаги умумий тушунчалар. Полимерлар нанотехнологияда.

III. Лаборатория машғулотлари буйича кўрсатма ва тавсиялар

Лаборатория машғулотлари учун қуйидаги мавзулар тавсия этилади:

Полимерланиш реакциялари

1). Стиролнинг полимерланиш кинетикасини ўрганиш
2). Метилметакрилатни инициаторни турли концентрацияларида полимерланиши
3). Мономер концентрациясини полимерланиш тезлигига таъсири
4). Бутилметакрилатнинг радикал полимерланишида иницирлаш тезлигини аниқлаш
5). Стиролнинг эритмада полимерланиши
6). Акрилонитрилнинг оксидланиш-қайтарилиш инициатори билан полимерланиши
7). Стиролнинг мунчоқсимон полимерланиши
8). Стиролни массада полимерланиш кинетикаси
9). Метилметакрилатни турли эритувчиларда полимерланиши
10). Метилметакрилатни массада турли хароратларда полимерланиши
11). Стиролнинг катион полимерланиши

Сополимерланиш реакцияси

1). Стиролни метакрил кислотаси билан сополимерланиши
2). Метиламеткрилатни мекакрил кислотаси билан сополимерланиши
3). Таркиб бўйича бир жинсли сополимерларнинг олиниши
4). Стирол билан метакрил кислотасини турли эритувчилар иштирокида сополимерланиши
5). Метилметакрилат билан метакрил кислотасини турли даражада сополимерланиши
6). Мономерларнинг турли нисбатларида стиролни акрил кислотаси билан сополимерланиши

Поликонденсатланиш реакцияси

1). Фтал ангидридини глицирин билан поликонденсатланиши
2). Фтал ангидридини этиленгликол билан поликонденсатланиши
3). Адипин кислотасини этиленгликол билан поликонденсатланиши
4). Лимон кислотасини этиленгликол билан поликонденсатланиши
5). Фенолни бензальдегид билан поликонденсатланиши
6). Гексаметилендиаминнинг адипин кислотаси билан

поликонденсатланиши
7). Чизиқсимон полиуретаннинг олиниши
8). Эпоксид смаласини олиниши
9). Мочевинани формальдегид билан поликонденсатланиши
10). Фенолни формальдегид билан поликонденсатланиши

Полимерларнинг кимёвий хоссалари

1).Стиролни малиен ангидриди билан сополимерининг ишқорий гидролизи
2). Полиакриламид гидролизини ишқорнинг ва полимернинг турли концентрацияларида ўрганиш
3). Турли хароратларда полиакриламиднинг ишқорий гидролизи
4). Целлюлоза ацетатлари таркибидаги ацетил гурухлар миқдорини аниқлаш
5). Полиакрилонитрил (Нитрон) толасининг қисман гидролизи
6). Полиакрилонитрил (Нитрон) толаси асосида толасимон анионит олиш
7). Полиакрилонитрил (Нитрон) толасини гидроксиламин билан кимёвий ўзгариши
8). Полиакриламид ва акриламиднинг ишқорий гидролизи
9). Поливинилацетатнинг алкоголизи
10). Полвинил спиртини сирка ангидриди билан этерификациялаш
11). Полвинил спиртини формальдегид билан ацеталлаш

Деструкция

1). Поливинил хлориднинг термик деструкцияси
2). Полиамидларнинг гидролитик деструкцияси
3). Полимерларнинг термооксидланиш деструкцияси
4). Поливинил спиртинининг оксидланиш деструкцияси
5). Турли хароратларда полиакриламиднинг эритмада деструкциясини ўрганиш
6). Полиакриламиднинг эритмада деструкцияланиши

Полимер эритмаларининг физик-кимёвий хоссалари

1). Тўрсимон полимерларнинг бўкиш тезлигига эритувчи табиатининг таъсири
2). Чокланган полимер тўрининг баъзи бир структуравий параметрларини мувозанатли бўкиш даражаси бўйича бахолаш
3). Полимерларнинг эриш критик хароратларидан Θ хароратини аниқлаш
4). Полимер эритмаларининг реологик хоссаларини ўрганиш

Полимерларнинг молекуляр массаси ва молекуляр массавий тақсимланиши

1). Полиамидларнинг молекуляр массасини аниқлаш
2). Полимерларнинг молекуляр массасини вискозиметрик усулда аниқлаш
3). Полимерларнинг молекуляр массасини криоскопик усулда аниқлаш
4). Полимерларнинг молекуляр массасини осмометрик усулда аниқлаш
5). Полиэфирларнинг молекуляр массасини аниқлаш

6). Эпоксид смолаларининг молекуляр массасини аниқлаш

7). Бўлаклаб чўктириш усули билан полимерларнинг молекуляр – массавий тақсимланишини аниқлаш

8). Полимерларнинг молекуляр –массавий тақсимланишини бўлаклаб эритиш усули билан аниқлаш

Полиэлектролитларнинг физик-кимёвий хоссалари

1). Катионит ва анионитларнинг статик алмашиниш сиғимини аниқлаш

2). Полиамфолитнинг изоэлектрик нуқтасини аниқлаш

3). Полиэлектролитни сувли ва тузли эритмаларининг гидродинамик хоссалари

4). Полимер ва қуйимолекуляр кислотанинг ионланиш константасини аниқлаш

5). Полиэлектролит макромолекулалари орасидаги кооператив реакциялар

Изоҳ: *Фаннинг ишчи дастурини шакллантириш жараёнида ўқув режада кўрсатилган соат ҳажмига мос ҳолда мавзулар танлаб юқорида тавсия этилган мавзулардан исталган 8 таси берилиши мумкин.*

IV. Мустақил таълим ва мустақил ишлар

Мустақил таълим учун тавсия этиладиган мавзулар.

1. Карбозанжирли ва гетерозанжирли полимернинг асосий вакиллари. Олиниши ва ишлатилиши.
2. Ўзбекистонда кўп тоннажли полимерлар саноатини ривожланиши ва имкониятлари.
3. Полимерланиш реакцияси тезлигини бошқариш имкониятлари.
4. Инициранлиш тезлигини ва бошқа кинетик кўрсатгич (C_M, C_S, C_P ва х.к.) ларни ҳисоблаш усуллари.
5. Сополимерлаш константаларини ҳисоблаш усуллари.
6. Ион-координацион полимерланишнинг афзаликлари.
7. Поликонденсацион усулда олинадиган саноат полимерлари.
8. Юқори молекуляр бирикмалар макромолекулалари букулувчанлигини бахолаш усуллари.
9. Полимер эритмаларнинг критик хароратлари.
10. Полимер материалларни мустахкамлигини ошириш йўллари..

Мустақил ўздаштириладиган мавзулар бўйича талабалар томонидан рефератлар тайёрлаш ва уни тақдимот қилиш тавсия этилади.

Изоҳ. *Мустақил таълим учун тавсия этилган мавзуларнинг соатлари лаборатория ва семинар машғулотларига тайёргарлик кўриш соатларидан ортиб қолган соатлар ҳажмидан келиб чиққан ҳолда белгиланади.*

3.

V. Фан ўқитилишининг натижалари (шаклланадиган компетенциялар)

Фанни ўзлаштириш натижасида талаба:

- полимерлар ва уларнинг муҳим вакилларини; полимерларни

	молекуляр- массавий тавсифлари; полимерлар синтези; полимерларни физик-кимёси; полимер эритмалар назарияси; полимерларни структураси ва физик-механик хоссалари; полимерларни кимёвий хоссалари; полимерларни деструкцияси ва уларни стабиллаш; полимерлар кимёсининг ҳозирги замон ютуқлари хақидаги ***тасаввурга эга бўлиши;*** - полимерларни синтез қила олиш; полимер эритмаларни тайёрлаш ва тозалай олиш; полимерлар молекуляр массаларини аниқлай олиш; полиэлектролитларнинг физик-кимёвий хоссаларини текшира олиш; полимерларнинг кимёвий хоссаларини тадқиқ қилиш ***кўникмаларига эга бўлиши;*** - полимерларнинг тирик табиатдаги роли ва уларнинг кимёвий материаллар сифатидаги ахамиятини англаш; полимерлар синтез қилиш усуллари ва механизмлари бўйича; макромолекулаларнинг букилувчанлигини анқлаш; полимерларнгинг кимёвий ўзгартириш; полимерлар олиш ***малакаларига эга бўлиши керак.***
4.	**VI. Таълим технологиялари ва методлари:** • маърузалар; • интерфаол кейс-стадилар; • гурухларда ишлаш; • тақдимотларни қилиш; • индивидуал лойиҳалар; • жамоа бўлиб ишлаш ва ҳимоя қилиш учун лойиҳалар.
5.	**VII. Кредитларни олиш учун талаблар:** Фанга оид назарий ва услубий тушунчаларни тўла ўзлаштириш, таҳлил натижаларини тўғри акс эттира олиш, ўрганилаётган жараёнлар ҳақида мустақил мушоҳада юритиш ва жорий, оралиқ назорат шаклларида берилган вазифа ва топшириқларни бажариш, якуний назорат бўйича ёзма ишни топшириш.
6.	**Асосий адабиётлар** 1. Christopher S. Brazel, Stephen L. Rosen. Fundamental principles of polymeric materials // Published by John Wiley & Sons, Inc., Hoboken, New Jersey. Published simultaneously in Canada, 2012. -427 p. 2. Sebastian Koltzenburg, Michael Maskos, Oskar Nuyken. Polymer Chemistry: Springer-Verlag Berlin Heidelberg 2017.- 584 p. 3. Babaev T.M. Yuqori molekulyar birikmalar. –T.: “Fan va texnologiya”, 2015, 528 bet. **Қўшимча адабиётлар** 1. Мирзиёев Ш.М.“Танқидий таҳлил, қатъий тартиб-интизом ва шахсий жавобгарлик - ҳар бир раҳбар фаолиятининг кундалик қоидаси бўлиши керак”. – Тошкент, “Ўзбекистон”. 2017. - 104 б. 2. Мирзиёев Ш.М. “Буюк келажагимизни мард ва олижаноб халқимиз билан бирга қурамиз” -Тошкент, “Ўзбекистон”. 2017. - 488 б. 3. Мирзиёев Ш.М. “Қонун устуворлиги ва инсон манфаатларини таъминлаш-юрт тараққиёти ва халқ фаровонлигининг гарови”.-Тошкент,

	"Ўзбекистон". 2017. - 48 б. 4. Мирзиёев Ш.М. "Миллий тикланишдан миллий юксалиш сари". – Тошкент, "Ёшлар нашриёт уйи". 2019. -158 бет. 5. Мирзиёв Ш.М. Танкидий тахлил, катъий тартиб-интизом ва шахсий жавобгарлик хар бир рахбар фаолиятининг кундалик коидаси бўлиши керак. Ўзбекистон Республикаси Вазирлар Махкамасининг 2016 йил якунлари ва 2017 йил истикболларига бағишланган мажлисидаги Ўзбекистон Республикаси президентининг нутқи. // Халқ сўзи газетаси. 2017 йил 16 январь, №11. 6. ЎзР ПҚ-2909. Олий таълим тизимини янада ривожлантириш чора-тадбирлари тўғрисида. Тошкент ш., 2017 й. 20 апрель. 7. Семчиков Ю. Высокомолекулярные соединия.М.:Асадема 2005, 367с. 8.Т. Бабаев ва бошқ. Юқори молекуляр бирикмалар ва полимер материаллар кимёси фанларидан лаборатория машғулотлари учун услубий қўлланма. Т.: Университет, 2019. 208 бет. 9. Тагер А.А. Физико-химия полимеров. Уч. пособие. М.: Химия, 1978. 10. Стрепихеев А.А. Деревицкая В.А. Основы химии высокомолекулярных соединений. Учебное пособие, М.: 1976. 11. Оудиан Дж. Основы химии полимеров. М.: Химия, 1978. 12. Шур А.М. Высокомолекулярные соединения. Учебник, М.: Высшая школа, 1981. **Ахборот манбаалари** 1. http://www.chem.msu.ru. 2. http://www.rushim.ru
7.	Фан дастури Олий ва ўрта махсус, касб-ҳунар таълими йўналишлари бўйича Ўқув-услубий бирлашмалар фаолиятини Мувофиқлаштирувчи Кенгашнинг 2020 йил 29 августдаги 4-сонли-сонли баённомаси билан маъқулланган. Ўзбекистон Республикаси Олий ва ўрта махсус таълим вазирлигининг 2020 йил 29 августдаги 452 - сонли буйруғи сонли буйруғи билан маъқулланган фан дастурларини таянч олий таълим муассасаси томонидан тасдиқлашга розилик берилган.
8.	**Фан/модуль учун маъсулар:** М.Г.Мухамедиев - ЎзМУ, "Полимерлар кимёси" кафедраси профессори, к.ф.д., профессор. Д.А.Гафурова-ЎзМУ,"Полимерлар кимёси" кафедра мудири, к.ф.д., доц.
9.	**Такризчилар:** Сманова З.А. - Ўзбекистон Миллий университети кафедра мудири, кимё фанлари доктори, професор; Ихтиярова Г.А. - Тошкент давлат техника университети кафедра мудири, кимё фанлари доктори, профессор.

MINISTRY OF HIGHER EDUCATION, SCIENCE AND
INNOVATION OF REPUBLIC OF UZBEKISTAN

NAMANGAN STATE UNIVERSITY
ORGANIC CHEMISTRY DEPARTMENT

«APPROVED»
Vice Rector for Academic
Affairs D. Holmatov

«___» _____________ *2023 y*

WORKING TRAINING PROGRAM BY SUBJECT

CHEMISTRY OF HIGH MOLECULAR COMPOUNDS

For 3 rd year daytime education

Area of Knowledge:	100000-natural subjects
Area of Education:	140000-Physic and natural subjects
Bachelor Direction:	60530100-Chemistry (daytime)

NAMANGAN – 2023

<table>
<tr><td colspan="2">Subject/Code module
YMB 1610</td><td>Study year
2023-2024</td><td>Term
5-6</td><td colspan="2">ECST-Credits
10 (6/4)</td></tr>
<tr><td colspan="2">Subject/Module type
Elective</td><td colspan="2">Study Language
English</td><td colspan="2">Weekly Lesson Hours
5 term - 4 hours
6 term- 4 hours</td></tr>
<tr><td rowspan="2">1</td><td colspan="2">Subject name</td><td>Audience training (hours)</td><td>Independent study (hours)</td><td>Total load (hours)</td></tr>
<tr><td colspan="2">Chemistry of high molecular weight compounds</td><td>120</td><td>180</td><td>300</td></tr>
</table>

I. SUBJECT CONTENT

The content of the subject is to give an idea to students about the sizes of polymer molecules and the causes of the chain structure. Explain to students the distinctive properties of polymers from low molecular weight.

The task of the subject is to give knowledge about the difference in polymers from low-molecular compounds, explain to students special properties of polymers, synthesis of polymers and physic-chemical properties, property of polymer solutions, obtaining new types of polymers.

II. MAIN THEORETICAL PART (LECTURES)

II.I. Content of Subject:

Lecture 1. Introduction. Basic concept and characteristics.
Basic concept, high-molecular compounds, oligomers, polymers. Macromolecule and its chemical link. The degree of polymerization and the length of the chain. The role of polymers in living nature and the importance as a chemical material. History of the development of the science of polymers. The contribution of scientists of Uzbekistan in the development of science and the subject of polymer chemistry.

Lecture 2. Classification of polymers and their main representatives.
Classification of polymers in dependence of appearance, chemical composition, main chain, link. Natural and synthetic polymers. Organic and inorganic polymers. Linear, branched and crosslinked polymers. Homopolymers, copolymers, block

copolymers. Homochain and heterochain polymers.

Lecture 3. Chemical classification of polymers.

Polymers and copolymers of monoolefins and their derivatives. Polyesters. Polyacetals. Polyamides, polyurethanes, polysaccharides, proteins, nucleic acids. Polysiloxanes.

Lecture 4. The concept of the molecular-mass characteristics of polymers.

Molecular-mass polymers, molecular weight distribution and the concept of the average molecular weight. Methods of fractionation.

Lecture 5. Synthesis of polymers. Radical polymerization.

Basic methods for the synthesis of polymers. Chain and step polymerization. Initiation in radical polymerization. Photochemical polymerization. Initiators. Radiation and thermal polymerization. Stages of radical polymerization. Development, breakage, chain transfer reactions. The length of the kinetic chain and factors affecting it. Inhibitor.

Lecture 6. Kinetics of radical polymerization.

Factors affecting the kinetics of radical polymerization. General formula for the kinetics of radical polymerization.

Lecture 7. Thermodynamics of polymerization.

Enthalpy and entropy changes in radical polymerization. Influence of the chemical structure of the monomer on polymerization. Polymerization at high convention. Effect of the chemical structure of the monomer on polymerization. Polymerization with high convention. The relationship between the reactivity of a radical and a monomer. The activation energy is the addition of radicals to the double bond of the monomer.

Lecture 8. Copolymerization reactions.

Composite equations of copolymerization. Constant value of copolymerization and methods for their determination. Q-e scheme of Alfray-Price.

Lecture 9. Calculations using copolymerization constants.

Copolymerization constants and methods for their determination. Q—e scheme of Alfrey-Price. Compositional heterogeneity of copolymers in composition. Microstructure of the copolymer chain.

Lecture 10. Ionic polymerization.

Cationic polymerization. Cationic polymerization reactions. Co-catalysts and joint catalysts.

Lecture 11. Anionic polymerization.

Anionic polymerization catchers. Coordination-ionic polymerization. Ziegler-Natta catalysts. Practical methods of polymerization.

Lecture 12. Polycondensation reactions.

Types of polycondensation reaction. The direction of polycondensation. Influence of temperature on polycondensation. Equilibrium polycondensation. The Carothers equation. Korshak's non-equivalence rules.

Lecture 13. Factors affecting the molecular weight during polycondensation. Carothers equation. Korshak's non-equivalence rules. Destructive reactions during polycondensation. Transformation of cyclic compounds into linear polymer. Phased (migratory) polymerization. Reactions: hydrolysis, alcolysis, acidolysis, periamidation, transesterification.

Lecture 14. Methods for obtaining polymers in industry.

Polymerization in solution, block and solid phase. Emulsion and suspension polymerization. Polycondensation in solution, mass and interfacial medium.

Lecture 15. Physical chemistry of polymers and their solutions. **Flexibility of polymers.**

Configuration isomerism and configuration of macromolecules. Conformational isomerism and conformation of macromolecules. Possibilities of internal rotations and flexibility of a macromolecule. The concept of a statistical segment. Coon segment. Kinetic and thermodynamic flexibility and methods for their determination.

Lecture 16. Supramolecular structure of polymers.

Amorphous and crystalline polymers. Features of the physical properties of polymers. relaxation properties. Phase properties of polymers. Factors affecting the crystallization of polymer.

Lecture 17. Physical states of polymers.

Dependence of the glassy, highly elastic and viscous-fluid state on the molecular weight of the polymer.

Lecture 18. Strength of polymers.

Mechanical properties of crystalline and amorphous polymers. Strength of polymers and operational properties. Plasticization of polymers. Plasticization mechanism. Requirements for plasticizers. Plasticization of polymers with another polymer.

Lecture 19. Theory of polymer solutions.

History of the development of the theory of solutions. True and real solutions. Solubility of polymers and factors affecting it. Thermodynamic evaluation of solubility.

Lecture 20. The process of dissolving polymers.

Phase diagrams for polymer-solvent systems. Swelling of polymers. Swelling kinetics. Association and solvation of polymer solutions.

Lecture 21. Hydrodynamic properties of polymer solutions.

Hydrodynamic properties of polymer solutions. Relative, reduced and intrinsic viscosity. Relationship between molecular weight and intrinsic viscosity.

Lecture 22. Methods for determining the molecular weight of polymers.

Methods for determining the shape and size of macromolecules in solution. Sedimentation and diffusion, light scattering method.

Lecture 23. Concentrated polymer solutions.

Viscosity of concentrated solutions and hysteresis. Gelation and jelly.

Lecture 24. Polyelectrolytes. Classification of polyelectrolytes.

Specific properties of polyelectrolyte solutions. Polyampholytes. Isoelectric point. Proteins are an example of amphoteric polyelectrolytes. Hydrodynamic properties of polyelectrolytes.

Lecture 25. Ionic equilibrium in polyelectrolytes.

Potentiometric titration of polyelectrolytes. G-singularity of the Henderson-Hasselbach equation for polyelectrolytes. interpolymer complexes. Practical value of polyelectrolytes. Ion exchange polymers.

Lecture 26. Chemical properties of polymers.

Types of chemical properties of polymers. Chemical properties of functional groups. Polymeranological and intramolecular reactions. Their mechanism and kinetics. The specifics of the reactivity of functional groups: local retention, configuration, conformation of macromolecules and the influence of the supramolecular structure of the polymer, neighbor effect, concentration and electrostatic effects.

Lecture 27. Intermacromolecular reactions.

Chemical modification of polymers. Vulcanization of rubber. Preparation and properties of block and graft copolymers.

Lecture 28. Destruction of polymers.

Reactions leading to a decrease in the degree of polymerization. Destruction. Destruction under the influence of chemical agents. Physical destruction. Destruction mechanism. Aging of polymers. Destruction under the influence of air, rays, radiation.

Lecture 29. Methods for stabilizing polymers.

Substances that accelerate and slow down the destruction. Methods for stabilizing polymers. Stabilizers and requirements for them.

Lecture 30. Polymer composite materials, basic concepts of polymers with specific properties. Polymers in nanotechnology.

II.2. Distribution of lecture topics

№	Topics	Hours
	Term V	2
1	Introduction. Basic concept and characteristics.	2
2	Classification of polymers	2
3	Chemical classification of polymers	2
4	The concept of the molecular-mass characteristics of polymers.	2
5	Synthesis of polymers. Radical polymerization	2
6	Kinetics of radical polymerization	2
7	Thermodynamics of polymerization	2
8	Copolymerization reactions	2
9	Calculations using copolymerization constants	2
10	Ionic polymerization	2
11	Anionic polymerization	2

12	Polycondensation reactions	2
13	Factors affecting the molecular weight during polycondensation	2
14	Methods for obtaining polymers in industry	2
15	Physical chemistry of polymers and their solutions. Flexibility of polymers	2
TOTAL		**30**
VI- term		
16	Supramolecular structure of polymers	2
17	Physical states of polymers	2
18	Strength of polymers.	2
19	Theory of polymer solutions	2
20	The process of dissolving polymers	2
21	Hydrodynamic properties of polymer solution	2
22	Methods for determining the molecular weight of polymers	2
23	Polymer gels	2
24	Polyelectrolytes	2
25	Ionic equilibrium in polyelectrolytes	2
26	Chemical properties of polymers	2
27	Intermacromolecular reactions	2
28	Destruction of polymers	2
29	Methods for stabilizing polymers	2
30	Low-tonnage polymer materials	2
Total		**30**
TOTAL HOURS		**60**

III.2. DISTRIBUTION OF LABORATORY TOPICS			
V-term			
1	**Polymerization reaction**	Study of the kinetics of styrene polymerization	**2**
		Study of the kinetics of styrene polymerization	**2**
		Polymerization of methyl methacrylate at	**2**

		various initiator concentrations	
		Polymerization of methyl methacrylate at various initiator concentrations	**2**
2	**Copolymerization reaction**	Copolymerization of styrene with methacrylic acid	**2**
		Copolymerization of styrene with methacrylic acid	**2**
		Copolymerization of styrene with methacrylic acid	**2**
3	**Polycondensation reaction**	Polycondensation of citric acid with ethylene glycol	**2**
		Polycondensation of citric acid with ethylene glycol	**2**
		Polycondensation of phenol with formaldehyde	**2**
		Polycondensation of phenol with formaldehyde	**2**
4	**Chemical properties of polymers**	Partial hydrolysis of polyacrylonitrile (nitron) fiber	**2**
		Partial hydrolysis of polyacrylonitrile (nitron) fiber	**2**
		Alkagolysis of polyvinyl acetate	**2**
		Alkagolysis of polyvinyl acetate	**2**
		TOTAL	**30**
		VI- term	
5	**Destruction**	Thermal destruction of polyvinyl chloride	**2**
		Thermal destruction of polyvinyl chloride	**2**
		Hydrolytic degradation of polyamides	**2**
		Hydrolytic degradation of polyamides	**2**
6	**Physical and chemical properties**	Influence of the Nature of the Solvent on the Swelling Rate of Cross-linked Polymers	**2**

	of polymer solutions	Influence of the Nature of the Solvent on the Swelling Rate of Cross-linked Polymers	**2**
		Influence of the Nature of the Solvent on the Swelling Rate of Cross-linked Polymers	**2**
		Influence of the Nature of the Solvent on the Swelling Rate of Cross-linked Polymers	**2**
7	**Molecular weight and molecular weight distribution of polymers**	Determination of the molecular weight of polymers by the viscometric methods	**2**
		Determination of the molecular weight of polymers by the viscometric methods	**2**
		Determination of the molecular weight of polymers by the viscometric methods	**2**
		Determination of the molecular weight of polymers by the viscometric methods	**2**
8	**Physico-chemical properties of polyelectrolytes**	Determination of the isoelectric point of polyampholytes	**2**
		Determination of the isoelectric point of polyampholytes	**2**
		Determination of the isoelectric point of polyampholytes	**2**
Total			**30**

IV. INDEPENDENT EDUCATION AND INDEPENDENT WORK	
№	**Subject of independent education**
1	The main representatives of carbon chain and heterochain polymers. Application.
2	Development and opportunities for the production of multi-tonnage polymers in Uzbekistan.
3	Possibilities of controlling the rate of polymerization reaction.
4	Methods for calculating the acceleration rate and other kinetic indicators (Cm,

	Cs, Cp, etc.).
5	Methods for calculating copolymerization constants
6	Advantages of ion-coordination polymerization
7	Industrial polymers based on polycondensation
VI-term	
8	Methods for assessing the flexibility of macromolecules of macromolecular compounds
9	Critical temperatures of polymer solutions
10	Ways to increase the strength of polymeric materials

V. RESULTS OF SCIENCE EDUCATION (COMPETENCIES TO BE FORMED)

As a result of mastering the subject, the student:

- polymers and their important representatives; molecular weight characteristics of polymers; polymer synthesis; physical chemistry of polymers; theory of polymer solutions; structure and physical and mechanical properties of polymers; chemical properties of polymers; destruction of polymers and their stabilization; should have an idea of modern achievements in polymer chemistry;
- able to synthesize polymers; be able to prepare and purify polymer solutions; be able to determine the molecular weight of polymers; check the physical and chemical properties of polyelectrolytes; have the skills to study the chemical properties of polymers;

Understanding the role of polymers in wildlife and their importance as chemical materials; on methods and mechanisms of polymer synthesis; determine the flexibility of macromolecules; chemical modification of polymers; must have skills in obtaining polymers.

VI. EDUCATIONAL TECHNOLOGIES AND METHODS

- ✓ lectures;
- ✓ interactive case studies;
- ✓ logical thinking, quick questions and answers;
- ✓ work in groups;
- ✓ preparation of presentations;
- ✓ individual projects;
- ✓ projects for teamwork and protection

VII. REQUIREMENTS FOR OBTAINING CREDITS

Credits allocated to science are provided to students in case of positive results from the types of control for each semester.

Intermediate (IC) and final (FC) control types are used to assess students' knowledge of science. Evaluation by control types: 5 - "excellent", 4 - "good", 3 - "satisfactory", 2 - "unsatisfactory" assessment criteria.

Midterm control is conducted once per semester in the form of oral or written work.

During the semesters, students are regularly evaluated and graded on each subject in practical (seminar) classes. In this case, the student's timely and complete completion of practical (laboratory) training and independent educational tasks, as well as his activity in training are taken into account.

Also, the grades received on practical (laboratory) training and independent educational tasks are taken into account in the evaluation by the type of interim control. In this case, the average of the grades obtained during each intermediate control type is re-averaged with the grade obtained from the intermediate control type.

The grade obtained from the intermediate controls is recorded in the record as the result of the intermediate control.

The final control type is conducted at the end of semesters in the form of oral or written work according to the approved schedule.

In intermediate (IC) and final (FC) control types:

A student makes independent conclusions and decisions, can think creatively, observes independently, can apply the acquired knowledge in practice, understands the essence of science (topic), knows, can express, tell, and is considered to have an idea about science (topic) – **5 (excellent) grades;**

When the student conducts independent observation, can apply the acquired knowledge in practice, understands the essence of the science (topic), knows, can express, tell and has an idea about the science (topic) - **4 (good) grade**;

When the student is able to apply the acquired knowledge in practice, understands the essence of the science (subject), knows, can express, tell and has an idea about the science (subject) - **3 (satisfactory) grade;**

When it is considered that the student has not mastered the science program, does not understand the essence of the science (topic) and does not have an idea about the science (topic) - he is evaluated with a grade of **2 (unsatisfactory**)

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Main literature

1. Christopher S. Brazel, Stephen L. Rosen. Fundamental principles of polymeric materials // Published by John Wiley & Sons, Inc., Hoboken, New Jersey. Published simultaneously in Canada, 2012. -427 p.
2. Sebastian Koltzenburg, Michael Maskos, Oskar Nuyken. Polimer Chtmistry: Springer-Verlag Berlin Heidelberg. 2017. -584 p.
3. Babaev T.M. Yuqori molekulyar birikmalar. –T.: “Fan va texnologiya”, 2015, 528 bet

Additional literature

14. Мирзиёев Ш.М. “Тарқидий таҳлил, қатъий тартиб-интизом ва шахсий жавобгарлик – ҳар бир раҳбар фаолиятининг кундалик қоидаси бўлиши керак”. –Тошкент, “Ўзбекистон”. 2017. -104 б.
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16. Мирзиёев Ш.М. Қонун устуворлиги ва инсон манфаатларини таъминлаш юрт тараққиёти ва халқ фаровонлигининг гарови. “Ўзбекистон” НМИУ, 2017. – 48 б.
17. Мирзиёев Ш.М. “Миллий тикланишдан миллий юксалиш сари”. Тошкент. “Ёшлар нашриёт уйи”. 2019. – 158 б.
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21. Мусаев У.Н., Бабаев Т.М., Курбанов Ш.А., Хакимжонов Б.Ш., Мухамедиев М.Г. Полимерлар кимёсидан практикум. Т.: Университет, 2001.
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Information source

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2. https://www.chem. msu.ru.

Curriculum developed and approved by Namangan State University

- The curriculum was discussed and recommended for approval at the general meeting of the Department of “Organic Chemistry” the meeting No__ “___ “ June 2023.
- The curriculum was discussed and recommend for approval in the meeting No____ of the Faculty of Natural Sciences “____” July 2023-year.
- The curriculum of the subject was discussed and approved by the educational and methodological council of NamSU meeting No.___ “___" July 2023-year.

Subject /Responsible for the credit:

D. Xaydarova – NamSU, Associate Professor of the Department of Organic Chemistry, Doctor of Philosophy (PhD) in the field of chemical sciences.

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Taqrizchilar:

Sh.V.Abdullayev – NamSU, Professor of the Department of Organic Chemistry, Doctor of Chemical Sciences.

A.M.Karimov – NamSU, Associate Professor of the Department of Organic Chemistry, Doctor of Chemical Sciences.

CONTROL QUESTIONS

1. What is a polymer, monomer?
2. Give examples of polymers.
3. What is the difference between polymers and low molecular weight compounds?
4. What is an elementary link?
5. What is the degree of polymerization?
6. What is average molecular weight?
7. What is polydispersity?
8. What polymer fractionation methods do you know?
9. Classification of polymers.
10. Give examples of linear, branched and network polymers.
11. Explain the chemical classification of polymers.
12. Destructive reactions during polycondensation.
13. Chemical classification of polymers. Polymers and copolymers of monoolefins and their derivatives. Polyesters
14. Macromolecule and its chemical unit. Degree of polymerization and chain length
15. anionic polymerization. Anionic polymerization catalysts.
16. Kinetics of radical polymerization. Thermodynamics of polymerization.
17. Influence of the chemical structure of the monomer on polymerization.
18. Initiation in radical polymerization. Photochemical polymerization. Initiators.
19. transformationcyclic compounds on linear polymers.
20. Polymerization of diamines and dihalides.
21. copolymerization reactions. Composite equation of copolymerization.
22. Molecular-weight of polymers, molecular-weight distribution
23. The concept of average molecular weight. Fractionation methods.
24. The relationship between the reactivity of the radical and the monomer. The activation energy is the addition of radicals to the double bond of a monomer.
25. Coordination-ionic polymerization. Ziegler-Natta catalysts.
26. Polycondensation reactions. Types of polycondensation reaction. direction of polycondensation.
27. Influence of temperature on polycondensation. equilibrium polycondensation.
28. Destructive reactions during polycondensation. Staged (migration) polymerization.
29. Staged and chain polymerization. radical polymerization.
30. Organic and inorganic polymers. Linear, branched and cross-linked polymers.
31. natural and synthetic polymers. Homopolymers, copolymers, block copolymers.
32. The length of the kinetic chain and the influencing factors on it. Inhibitors.
33. Classification of polymers depending on appearance, chemical composition, main chain, link.
34. Basic methods for the synthesis of polymers.Radiation and thermal polymerization. Growth, termination and transfer reactions.
35. Basic concept, macromolecular compounds, oligomers, polymers.
36. Polymerization of cyclic compounds.
37. Classification of polymers and their main representatives. Homochain and heterochain polymers.

38. The history of the development of the science of polymers. The contribution of scientists of Uzbekistan in the development of science and the subject of chemistry of macromolecular compounds.
39. Constant value of copolymerization and methods for their determination.
40. Ionic polymerization reaction. Catalysts and co-catalysts.

Intermediate work in Naval Chemistry

Option 1

1. Basic concept, macromolecular compounds, oligomers, polymers.Polyesters. Polyacetals.
2. Macromolecule and its chemical link.
3. Chemicalclassification of polymers.

Option 2

1. Polymers and copolymers of monoolefins and theirThe role of polymers in wildlife and their importance as a chemical material.
2. History of the development of the science of polymers.
3.Molecular weight of polymers, molecular weight distribution and the concept of average molecular weight.

Option 3

1. The contribution of scientists of Uzbekistan to the development of science and the subject of chemistrymacromolecular compounds.
2. Reactions of growth, breakage and transmission.
3. Activation energy of addition of radicals to the double bond of the monomer.

Option 4

1.Classification of polymersdepending on appearance, chemical composition, main chain, link.
2. Degree of polymerization and chain length.
3. Radiation and thermal polymerization.

Option 5

1. Kinetics of radical polymerization. Thermodynamics of polymerization.
2. Relationship between the reactivity of the radical and the monomer.
3.Fractionation methods.

Option 6

1. Natural and synthetic polymers.
2. The length of the kinetic chain and the factors influencing it. Inhibitors.
3. Constant values of copolymerization and methods for their determination

Option 7

1. Linear, branched and cross-linked polymers.
2. Radical polymerization.
3. Initiators.

Option 8

1. Homopolymers, copolymers, block copolymers.
derivatives.
2. Influence of monomer structure on polymerization.Influence of the chemical structure of the monomer on polymerization.
3.Initiation in radical polymerization.

Option 9

1. Polyamides, polyurethanes, polysaccharides, proteins, nucleic acids. Polysiloxanes.
2. Copolymerization reactions. Composite equation of copolymerization.

3. Photochemical polymerization.

Option 10

1. Organic and inorganic polymers.
2. High convention polymerization.
3. Basic methods for the synthesis of polymers.Staged and chain polymerization.

Intermediate work in Naval Chemistry

Option number 1

1. Physical destruction
2. Glassy state of polymers
3. Physical and mechanical properties of polymers

Option number 2

1. Destruction
2. Supramolecular structure of polymers
3. Highly elastic state of polymers

Option number 3

1. Polyelectrolytes
2. Types of plasticizers
3. Relaxation

Option number 4

1. Three amorphous states of polymers
2. Requirements for plasticizers
3. Polymer-similar transformations

Option number 5

1. Chemical properties of polymers
2. Amorphous polymers
3. Intramolecular reactions

Option number 6

1. Hydrodynamic properties of polymer solutions
2. Scattering method
3. Classification of polyelectrolytes

Option number 7

1. Rheological properties of polymers
2. The rule of volumetric concentrations in the theory of plasticization
3. Isoelectric point of polyampholytes

Option number 8

1. Oxidative degradation
2. The concept of plasticizer compatibility
3. Reactivity of functional groups

Option number 9

1. The rule of molar concentrations in the theory of plasticization
2. Thermal-oxidative degradation
3. Syneresis

Option number 10

1. Phase states of polymers

2. Curing
3. Microencapsulation

Option number 11

1.Three amorphous states
2. Random destruction
3. Neighbor Effect

Option number 12

1. Structure formation of polymers
2. Difference between destruction and depolymerization
3.Plastification

Final work on the chemistry of macromolecular compounds

Option 1

1. Basic concept, macromolecular compounds, oligomers, polymers.Polyesters. Polyacetals.
2. Macromolecule and its chemical link.
3. Chemicalclassification of polymers.

Option 2

1. Polymers and copolymers
2. History of the development of the science of polymers.
3.Molecular weight of polymers, molecular weight distribution and the concept of average molecular weight.

Option 3

1. The contribution of scientists of Uzbekistan to the development of science and the subject of chemistrymacromolecular compounds.
2. Reactions of growth, breakage and transmission.
3. Activation energy of addition of radicals to the double bond of the monomer.

Option 4

1.Classification of polymersdepending on the origin, chemical composition, main chain, link.
2. Degree of polymerization and chain length.
3. Radiation and thermal polymerization.

Option 5

1. Kinetics of radical polymerization.
2.Polymerization of cyclic compounds.
3.Macromolecule and elementary link

Option 6

1. Natural and synthetic polymers.
2. The length of the kinetic chain and the factors influencing it. Inhibitors.
3. Copolymers and copolymerization

Option 7

1. Linear, branched and cross-linked polymers.
2. Radical polymerization.

3. Initiators.

Option 8

1. Homopolymers, copolymers, block copolymers.
derivatives.
2. Influence of monomer structure on polymerization.
3.Initiation in radical polymerization.

Option 9

1. Polyamides, polyurethanes, polysaccharides, proteins, nucleic acids. Polysiloxanes.
2. Copolymerization reactions.
3. Photochemical polymerization.

Option 10

1. Organic and inorganic polymers.
2. Catalysts for anionic polymerization. Ziegler-Natta catalysts.
3.Basic methods for the synthesis of polymers..

Option 11

1. Kinetics of radical polymerization.
2.Polymerization of cyclic compounds.
3.Macromolecule and elementary link

Option 12

1. Natural and synthetic polymers.
2. The length of the kinetic chain and the factors influencing it. Inhibitors.
3. Copolymers and copolymerization

TESTS
"Reactions of polymerization and polycondensation"

1. Polymerization reactions are characteristic of:
a) benzene b) propane
c) propylene d) acetic acid

2. Rubber is obtained by polymerization reaction:
a) isobutylene b) styrene
c) propylene d) butadiene -1.3
3. The polymerization reaction enters:
a) C4H10 b) CH2=CH-CH=CH2
c) C6H5-CH3 d) CH3-CH2CH=CH-CH2-CH3
4. Polystyrene is formed during polymerization:
a) CH3-CH=CH2 b) C6H5C2H3
c) C6H5CH=CH2 d) CH2=CH-CH3
|
CH3
5. Polypropylene -CH2-CH- is obtained by the reaction:
|
CH3
a) polycondensation b) polymerization
c) restoration d) splitting off

6. Polycondensation reaction is possible between:
a) CH2=CH-CH3 and C6H5OH b) CH3CH2NH2 and HCL
c) C6H5OH and HCHO d) H2NCH2COOH and NaOH

Plastics, rubbers, fibers
Test 1
1. Specify the names of macromolecular substances of natural origin:
a) polyethylene b) starch
c) glucose d) cellulose CH3
2. Mark the structural unit of polypropylene: |
a) -CH2-CH2-; b) - CH2- CH -; c) –CH2-CH-CH3; d) -CH2 -C -
| |
CH3 CH3
3. What geometric shape do glycogen macromolecules have?
a) linear; b) spatial (mesh); c) branched.
4. What statements regarding the properties of polymers are true?
a) all macromolecules of a given polymer consist of the same number of structural units
links;

b) polymers do not have a strictly defined melting point;
c) the polymer is characterized not by a certain, but by an average value of the molar mass;
d) the strength of polymers of a spatial structure is higher than that of linear polymers
buildings.

5. Of the listed substances, mark the plastics:
a) lavsan; b) polystyrene; c) polyvinyl chloride; 4) fiber.

6. How does an increase in the degree of its crystallinity affect the mechanical strength of a polymer?
a) mechanical strength increases; b) decreases; c) does not change.

7. How do the degrees of crystallinity of high and low polyethylene correlate with each other
pressure?
a) higher for high pressure polymer; b) are the same;
c) higher for low pressure polymer.

8. Which of the following polymers are thermoplastic?
a) polystyrene; b) textolite;
c) polyvinyl chloride; d) polypropylene.

9. Natural rubber is:
a) the cis form of the polybutadiene; b) trans-form of polybutadiene;
c) trans-form of polyisoprene; d) the cis form of the polyisoprene.

10. What is the degree of polymerization of polypropylene with an average molar mass
100000g/mol?
a) 2300; b) 2375; c) 2381; d) 2392.

Test 2

1. Which of the following fibers are chemical?
a) cotton b) viscose
c) lavsan d) wool

2. Which two of the following substances interact with each other to form a monomer used to produce lavsan fiber?
a) ethylene glycol b) glycerin
c) benzoic acid d) terephthalic acid

3. What polymers are produced by the polymerization reaction?
a) phenol-formaldehyde plastic b) kapron fiber
c) styrene-butadiene rubber d) polyethylene

4. The polymer, called "organic glass", is obtained by polymerization:
a) acrylonitrile b) styrene
c) methyl methacrylate d) propylene

5. How do the mass of a macromolecule (obtained as a result of polymerization) and the sum of the masses of the molecules that formed it relate to each other?
a) more than the mass of the macromolecule b) both masses are equal

c) the sum of the masses of individual molecules is greater

6. Specify fair statements:

a) the substances involved in the polymerization reaction must necessarily contain multiple bonds;

b) initiator and catalyst in polymerization processes are identical concepts;

c) the greater the difference in the value of the molar masses of macromolecules of the same

polymer, the wider the melting temperature range for it;

d) the strength of substances consisting of linear polymers increases with increase in the degree of polymerization

7. What fibers contain an amide bond?

a) lavsan b) acetate

c) anide d) nitrone

8. Synthetic fibers include:

a) linen b) copper-ammonia

c) anide d) nitrone

9. Specify the mass fraction of chlorine (%) in polyvinyl chloride:

a) 55.8 b) 56.8 c) 57.8 d) 58.8

10 Polypropylene macromolecules of a stereoregular structure have a geometric shape:

a) linear; b) spatial; c) branched

Test 3

1. What is the relationship between the mass of a macromolecule (obtained as a result of polycondensation) and the sum of the masses of the individual molecules that formed it?

a) the mass of the macromolecule is greater b) both masses are equal

c) the sum of the masses of the molecules is greater

2. What mandatory requirement must satisfy substances that enter into a polycondensation reaction involving only this substance?

a) the presence of one functional group in the molecule;

b) the presence of multiple bonds;

c) the presence of at least two functional groups in the molecule

3. Specify the formula of the substance resulting from the depolymerization of polymethyl methacrylate:

CH3 CH3 H
| | |
a) -CH2 -CH - b) -CH2 -C - O c) CH2= CO d) CH2= CO
| \ // \ // \ //
CL CCC
\ \ \
O–CH3 OCH3 OCH3

4. Which of the named polymers will be the least resistant to the action of acid and alkali solutions when heated?
a) polypropylene b) polyvinyl chloride
c) polyethylene d) polymethyl methacrylate
5. Which of the following fibers are artificial?
a) nitron b) woolen
c) viscose d) acetate
6. What fiber can be called polyester?
a) kapron b) nylon
c) lavsan d) nitron
7. What rubber is called divinyl?
a) stereoregular isoprene rubber
b) isoprene rubber with a trans-form of macromolecules
c) stereoregular butadiene rubber
d) butadiene-styrene
8. What rubbers are obtained by copolymerization?
a) divinyl b) butadiene-styrene
c) nitrile butadiene d) chloroprene

19. The average molar mass for Teflon is 300,000 g/mol. Specify the value of the degree of polymerization of this polymer:
a) 2000 b) 3000 c) 4000 d) 3500

Molecular - mass characteristics of polymers

1.To a mixture of two polymer fractions, consisting of N molecules with a number average degree of polymerization PN equal to 100 and N molecules with PN equal to 10000, another N molecules with PN equal to 10000 were added. (MW - weight average, MN - number average molecular weight). The A2/A1 ratio is:
1. 1 < A2/A1 < 2 2. 1 < A1/A2 < 2 3. A1/A2 > 2 4. A2/A1 > 2
2. For a mixture of two polymer fractions, consisting of N molecules with a number-average degree of polymerization PN equal to 100 and N molecules with PN equal to 10000, the polydispersity parameter A = MW/MN = 2. When adding N molecules with PN equal to 100, the value And it changes. To compensate for this change, it is necessary to add to the mixture of molecules with PN equal to 10,000 in an amount equal to: 1. N 2. N / 100 3. 100 N 4. N / 2
3. To a mixture of two polymer fractions, consisting of N molecules with a number-average degree of polymerization PN equal to 100 and N molecules with PN equal to 10000, another N molecules with PN equal to 100 were added. In this case, the polydispersity parameter A1 = MW/MN changed to A2 values (MW - weight average, MN - number average molecular weights). The A2/A1 ratio is:
1. A2/A1 > 2 2. A1/A2 > 2 3. 1 < A2/A1 < 2 4. 1 < A1/A2 < 2
4. The average molecular weight of a system consisting of 100 molecules with a mass of 100, 20 molecules with a mass of 500 and 50 molecules with a mass of 200 is 267. In this case, the average molecular weight is:
1. numeric 2. weight 3. viscous 4. z-average

5. The average molecular weight of a system consisting of 10 molecules with a mass of 4000, 40 molecules with a mass of 10000 and 50 molecules with a mass of 40000 is 24400. In this case, the average molecular weight is: 1. numerical 2. weight 3. viscous 4. z-average
6. The correct ratio between the MWD characteristics for a polydisperse polymer is (MW - weight average, MN - number average, MZ - z - average molecular weights)
1. MZ < MN < MW 2. MZ > MW > MN 3. MZ > MN > MW 4. MN > MW > MZ
7. The MW / MN ratio (MW - weight average, MN - number average molecular weight) for a system containing 2N molecules with a mass of 1, 2N molecules with a mass of 2, 7N molecules with a mass of 3, 2N molecules with a mass of 4, is described by the following inequality:
1. 1.0 < MW/MN < 1.2
2. 1.2 < MW/MN < 1.4
3. 1.4 < MW/MN < 1.6
4. 1.6 < MW/MN < 1.8
8. The number average molecular weight for a system containing N molecules with a mass of 1, N molecules with a mass of 2, 3N molecules with a mass of 3, 5N molecules with a mass of 4, 4N molecules with a mass of 5 and 2N molecules with a mass of 6 is equal to: 1. 4 .5 2. 3 3. 4 4. 3.5

9. The mass average molecular weight for a system containing N molecules with a mass of 1, 3N molecules with a mass of 2, 4N molecules with a mass of 3 and 2N molecules with a mass of 4 is:
1.3 2.3.5 3.4 4.2.5

10. Non-compliance with the law of composition constancy for polymers causes the presence of:
1. molecular weight distributions
2. different end groups
3. ramifications
4. in a chain of atoms of various nature

eleven. The molecular weight of polyvinylpyrrolidone with a degree of polymerization of 100 is (neglect end groups in the calculation): 1. 11200 2. 11100 3. 12500 4. 9700
12. The molecular weight of polydimethylsiloxane with a degree of polymerization of 100 is (neglect the end groups in the calculation): 1. 10400 2. 7400 3. 10600 4. 7200

13. The molecular weight of polyvinylidene fluoride with a degree of polymerization of 100 is (neglect the end groups in the calculation): 1. 6400 2. 4600 3. 10000 4. 3200

14. The molecular weight of polymethyl methacrylate with a degree of polymerization of 80 is (neglect the end groups in the calculation): 1. 6720 2. 8000 3. 8160 4. 6880

15. The molecular weight of poly-alpha-methylstyrene with a degree of polymerization of 50 is (neglect the end groups in the calculation): 1. 5900 2. 4900 3. 5200 4. 2100

16. The molecular weight of polyvinylene carbonate with a degree of polymerization of 1000 is (neglect the end groups in the calculation): 1. 92000 2. 86000 3. 72000 4. 78000

17. The molecular weight of polyvinyl acetate with a degree of polymerization of 1500 is:
1. 120000 2. 129000 3. 111000 4. 101000

18. If 1 g of polyethylene terephthalate (lavsan) with a degree of polymerization of 1000 contains N molecules of the substance, then the value of N is in the range (neglect end groups in the calculation):
1. 1 1018 < N < 2 1018
2. 2 1018 < N < 4 1018
3. 4 1018 < N < 6 1018
4. 8 1018 < N < 1019

19. If 1 g of polyhexamethylene adipamide (nylon-66) with a number average degree of polymerization of 1000 contains N molecules of the substance, then the value of N is in the range (neglect end groups in the calculation):
1. 1 1017 < N < 1018
2. 2 1018 < N < 3 1018
3. 3 1018 < N < 4 1018
4. 4 1018 < N < 5 1018

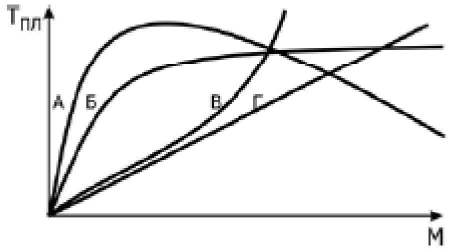
20. There is a mixture of 0.1 mol (per unit) of polymers: polypropylene, polychloroprene, polybutadiene and polystyrene. Bromine can react with this mixture (in the dark, under mild conditions, possible reactions of the end groups can be neglected) in an amount equal to:
1. 0.2 mol 2. 0.3 mol 3. 0.4 mol 4. 0.1 mol

21. If 1 g of cellulose with a number average degree of polymerization of 1000 contains N molecules of a substance, then the value of N is in the range (disregard the end groups in the calculation):
1. 3 1018 < N < 4 1018
2. 4 1018 < N < 5 1018
3. 2 1018 < N < 3 1018
4. 1 1017 < N < 1 1018

22. If 1 g of polyvinyl alcohol with a degree of polymerization of 1000 contains N molecules of the substance, then the value of N is in the range (disregard the end groups in the calculation):

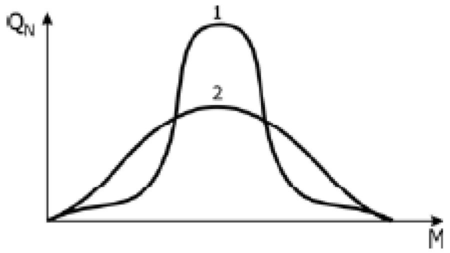
1. 5 1018 < N < 1 1019
2. 2 1018 < N < 5 1018
3. 1018 < N < 2 1018
4. 1019 < N < 2 1019

23. From the above curves of the dependence of the melting point of normal alkanes on the number of –CH2 groups in the chain (N) (the range of N changes up to 100000-1000000) corresponds to:



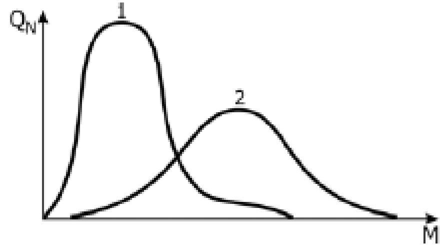
1. curve C 2. curve B 3. curve D 4. curve A

24. The figure shows QW - MWD mass functions of two polymer samples. The correct conclusion about the number average molecular weights MN of samples 1 and 2 is:



1. MN(1) < MN(2)
2. MN(1) > MN(2)
3. MN(1) = MN(2)
4. cannot be answered unambiguously

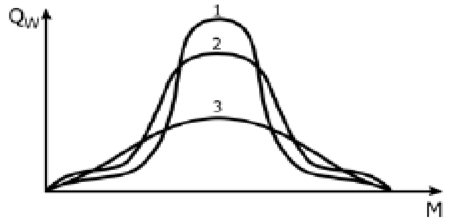
25. The figure shows QN - numerical functions of the MWD of two polymer samples. The correct conclusion about the weight average molecular weights MW of samples 1 and 2 is:



1. cannot be answered unambiguously

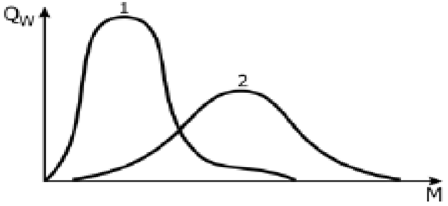
2. MW(1) < MW(2)
3. MW(1) > MW(2)
4. MW(1) = MW(2)

26. The figure shows QW - the mass function of the MWD of three polymers. The correct conclusion about the number average molecular weights MN of the three polymer samples is:



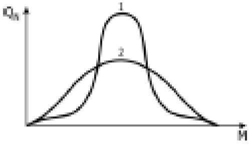
1. MN(1) < MN(2) < MN(3)
2. MN(1) = MN(2) = MN(3)
3. MN(1) > MN(2) > MN(3)
4. cannot be answered unambiguously

27. The figure shows QW - MWD mass functions of two polymer samples. The correct conclusion about the number average molecular weights MN of these samples is:



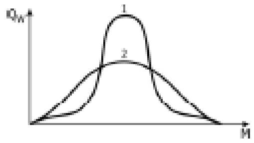
1. MN(1) < MN(2)
2. MN(1) > MN(2)
3. MN(1) = MN(2)
4. cannot be answered unambiguously

28. The figure shows QN - numerical functions of the MWD of two polymer samples. The correct conclusion about the weight average molecular weights MW of samples 1 and 2 is



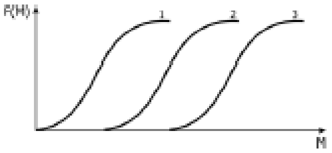
1. MW(1) > MW(2)
2. MW(1) < MW(2)
3. MW(1) = MW(2)
4. cannot be answered unambiguously

29. The figure shows QW - MWD mass functions of two polymer samples. The correct conclusion about the number average molecular weights MN of these samples is:



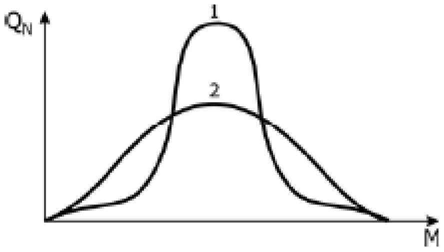
1. MN(1) > MN(2)
2. MN(1) < MN(2)
3. MN(1) = MN(2)
4. cannot be answered unambiguously

30. When considering the integral mass functions of the MMP - F (M), the correct conclusion about the average
The non-mass molecular weights MW of the three samples (1, 2, 3) is:



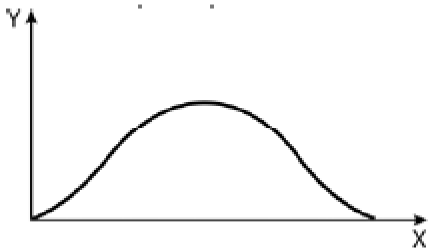
1. MW(1) > MW(2) > MW(3)
2. MW(1) = MW(2) = MW(3)
3. MW(1) < MW(2) < MW(3)
4. cannot be answered unambiguously

31. The figure shows QN - numerical functions of the MWD of two polymer fractions. The correct conclusion about the number average molecular weights (MN) of these fractions is:



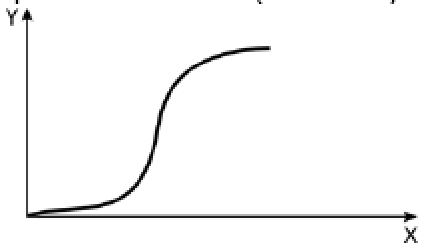
1. MN(1) = MN(2)
2. MN(1) < MN(2)
3. MN(1) > MN(2)
4. cannot be answered unambiguously

32. The differential numerical function of the molecular mass distribution has the form pre-
placed in the figure. The physical meaning of the parameters X and Y is (M is the molecular weight):



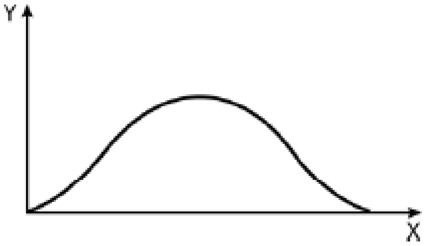
1. X - M, Y - mass fraction of molecules of mass less than or equal to M
2. X - M, Y - mass fraction of molecules of mass M
3. X - M, Y - number of molecules of mass M
4. X - M, Y - total mass of molecules of mass M

33. The integral mass function of the molecular mass distribution has the form shown in the figure. The physical meaning of the parameters X and Y is (M is the molecular weight):



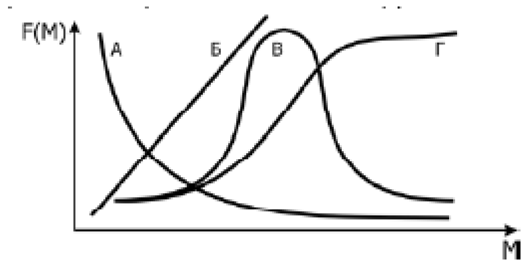
1. X - M, Y - mass fraction of molecules of mass less than or equal to M
2. X - M, Y - number of molecules of mass M
3. X - M, Y - mass fraction of molecules of mass M
4. X - M, Y - total mass of molecules of mass M

34. The differential mass function of the molecular mass distribution has the form preplaced in the figure. The physical meaning of the parameters X and Y is (M is the molecular weight):



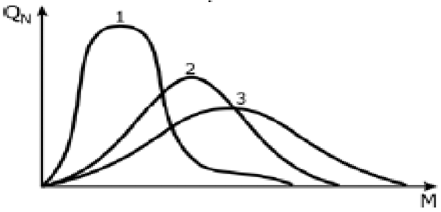
1. X - the numerical fraction of molecules of mass M, Y - M
2. X - M, Y - the numerical fraction of molecules of mass M
3. X - the numerical fraction of molecules with a mass less than or equal to M, Y - M
4. X - M, Y - the numerical fraction of molecules with a mass less than or equal to M

35. From the curves shown in the figure, the integral mass function of the MMP corresponds to:



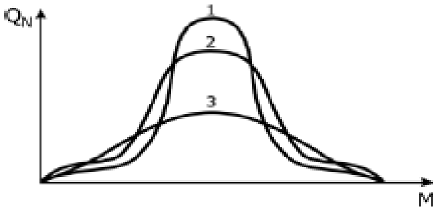
1. curve B 2. curve D 3. curve C 4. curve A

36. The figure shows QN - numerical functions of the MWD of three polymer samples. The correct conclusion about the weight average molecular weights MW of these samples is:



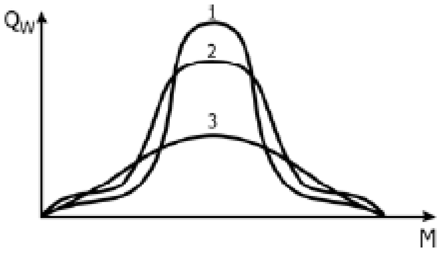
1. MW(1) > MW(2) > MW(3)
2. MW(1) < MW(2) < MW(3)
3. MW(1) = MW(2) = MW(3)
4. cannot be answered unambiguously

38. The figure shows QN - the numerical function of MWD for three polymers. The correct conclusion about the weight average molecular weights MW of the three polymer samples is:



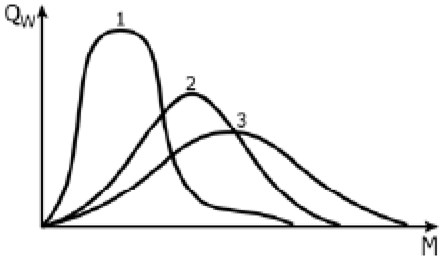
1. MW(1) < MW(2) < MW(3)
2. MW(1) > MW(2) > MW(3)
3. MW(1) = MW(2) = MW(3)
4. cannot be answered unambiguously

39. The figure shows QW - MWD mass function for three different polymers MW - average weight, MN - number average molecular weight. The correct conclusion about the values of the polydispersity parameter A=MW/MN is:



1. A1 > A2 > A3
2. A1 = A2 = A3
3. It is impossible to answer unambiguously
4. A1 < A2 < A3

40. The figure shows QW - MWD mass function for three polymers. MW - middleweight, MN
number average molecular weights. The correct conclusion about the values of the polydispersity parameter A=MW/MN is:



1. A1 > A2 > A3
2. A1 < A2 < A3
3. A1 = A2 = A3
4. cannot be answered unambiguously

2. Classification and structural formulas of basic polymers

2.1. Classification of polymers

1. Among the polymers listed below, heterochain ones are:
1. polymethyl methacrylate 2. cellulose 3. polyphenylene 4. polycaproamide
5. polyformaldehyde 6. polyethylene oxide 7. polyethylene terephthalate

2.Polycaproamide refers to:
1. linear polymers 2. carbon chain polymers 3. homochain polymers
4. heterochain polymers 5. polyacetals 6. polyamides 7. polyesters

3.Polyethylene oxide, polyethylene terephthalate and polyformaldehyde are classified as:
1. linear polymers 2. homochain polymers 3. carbon chain polymers
4. heterochain polymers 5. organoelement polymers 6. ladder polymers

4. Polymers: polyisobutylene, polymethyl methacrylate, polyethylene glycol terephthalate, polycaproamide, polyphosphonitrile chloride are combined into one group according to the following features:
1. organic 2. heterochain 3. organoelement 4. macromolecular 5. cross-linked

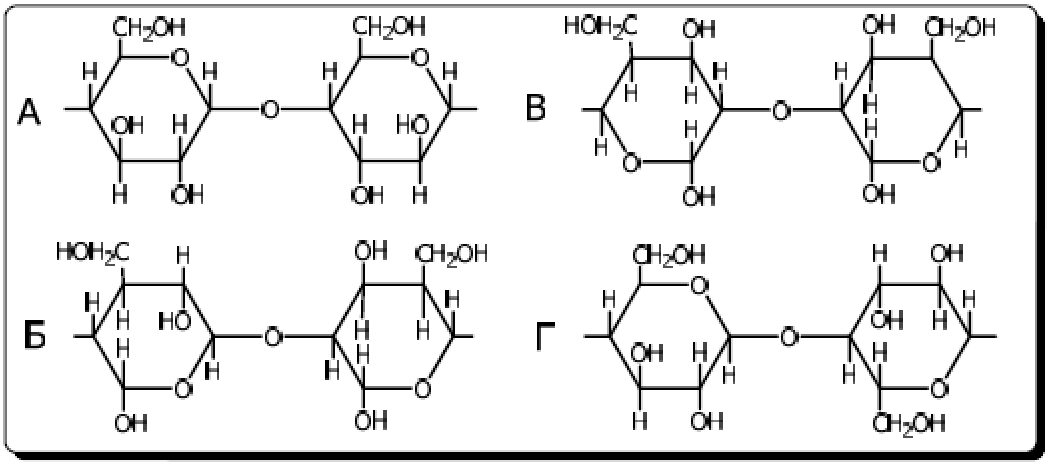
5. Polymers of the vinyl series are:
1. polypropylene 2. polyisobutylene 3. polystyrene 4. polymethyl methacrylate
5. polychloroprene 6. polycaproamide

6.Polymers: gutta-percha, polyvinylpyridine, plastic sulfur, diamond, are combined into one group according to the following features:
1. organoelement 2. natural 3. homochain 4. three-dimensional 5. heterochain
6. linear

7.Polyvinyl butyral belongs to the type of polymers:
1. linear 2. homochain 3. ladder 4. heterochain 5. organoelement

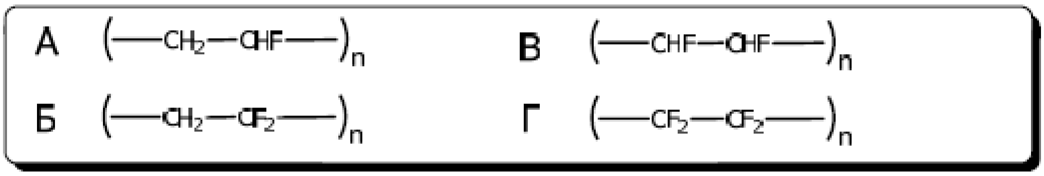
2.2. Structural formulas of basic polymers

1. Among the listed formulas, cellulose corresponds to:



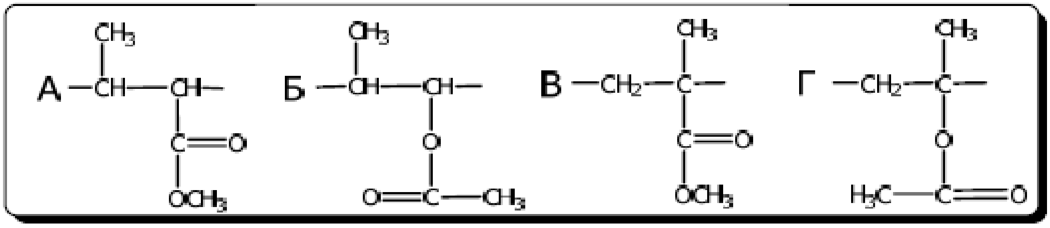
1. Formula D 2. Formula A 3. Formula B 4. Formula C

2.From the above formulas, the unit of polyvinylidene fluoride corresponds to:



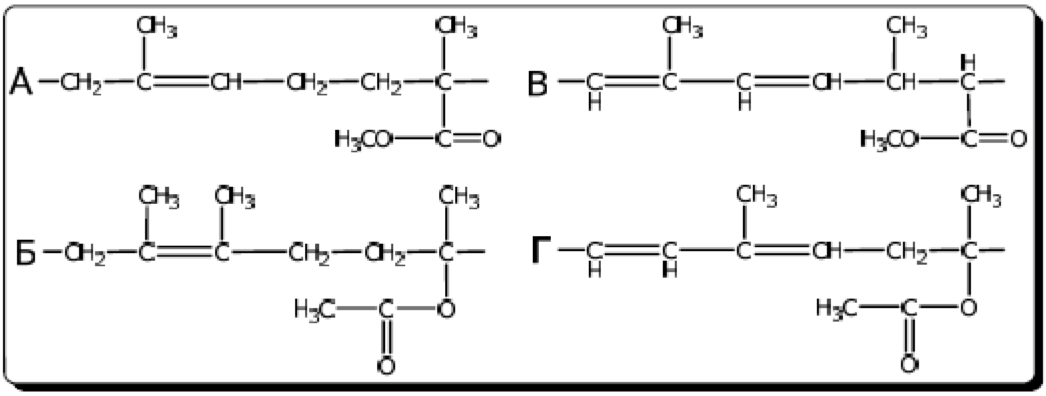
1. Formula D 2. Formula A 3. Formula B 4. Formula C

3. From the above formulas, the formula correctly reflects the structure of the polymethyl methacrylate unit:



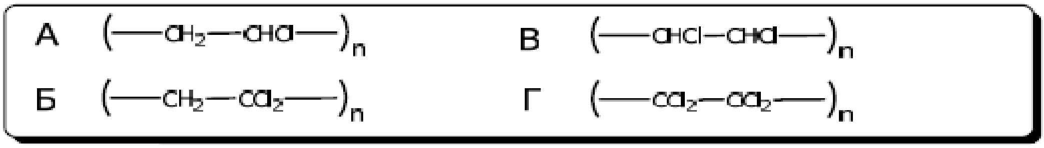
1. Formula D 2. Formula A 3. Formula B 4. Formula C

4. For the copolymer of isoprene with methyl methacrylate, the formula is valid:



1. Formula A 2. Formula B 3. Formula C 4. Formula D

5. The polyvinylidene chloride link corresponds to the formula:

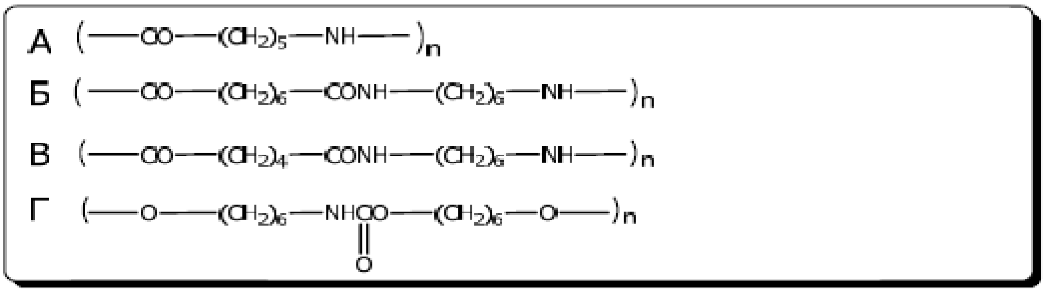


А $(-CH_2-CHCl-)_n$ В $(-CHCl-CHCl-)_n$

Б $(-CH_2-CCl_2-)_n$ Г $(-CCl_2-CCl_2-)_n$

1. formula C 2. formula B 3. formula D 4. formula A

6. Among the listed formulas, polyamide 6 corresponds to:



А $(-CO-(CH_2)_5-NH-)_n$

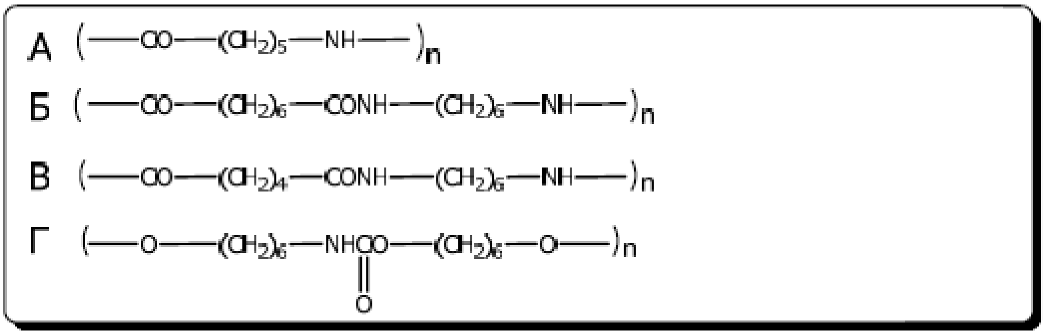
Б $(-CO-(CH_2)_6-CONH-(CH_2)_6-NH-)_n$

В $(-CO-(CH_2)_4-CONH-(CH_2)_6-NH-)_n$

Г $(-O-(CH_2)_6-NH\underset{\overset{\|}{O}}{C}O-(CH_2)_6-O-)_n$

1. Formula A 2. Formula B 3. Formula C 4. Formula D

7. Among the listed formulas, polyamide 6.6 corresponds to:



А $(-CO-(CH_2)_5-NH-)_n$

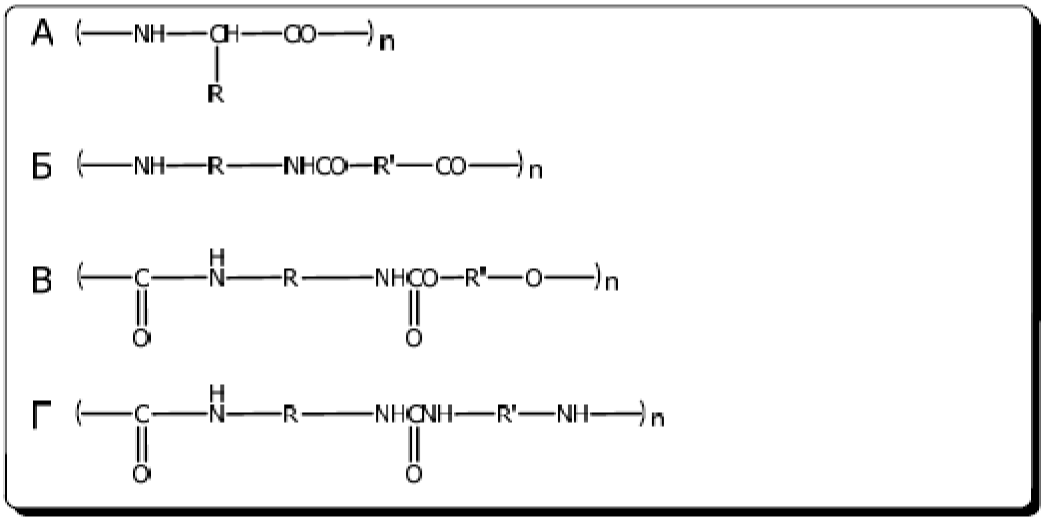
Б $(-CO-(CH_2)_6-CONH-(CH_2)_6-NH-)_n$

В $(-CO-(CH_2)_4-CONH-(CH_2)_6-NH-)_n$

Г $(-O-(CH_2)_6-NH\underset{\overset{\|}{O}}{C}O-(CH_2)_6-O-)_n$

1. Formula D 2. Formula C 3. Formula A 4. Formula B

8.Among the listed formulas, polyurethanes correspond to:



А $(-NH-\underset{\overset{|}{R}}{CH}-CO-)_n$

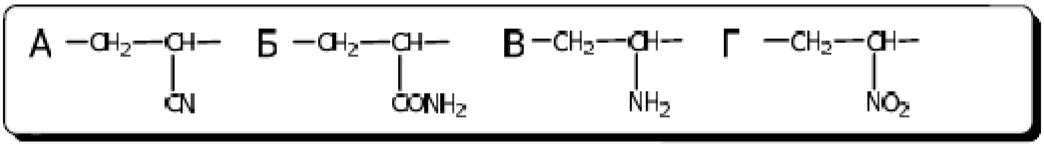
Б $(-NH-R-NHCO-R'-CO-)_n$

В $(-\underset{\overset{\|}{O}}{C}-\overset{H}{N}-R-NH\underset{\overset{\|}{O}}{C}O-R'-O-)_n$

Г $(-\underset{\overset{\|}{O}}{C}-\overset{H}{N}-R-NH\underset{\overset{\|}{O}}{C}NH-R'-NH-)_n$

1. Formula D 2. Formula A 3. Formula C 4. Formula B

9. Among the listed formulas, polyacrylamide corresponds to:

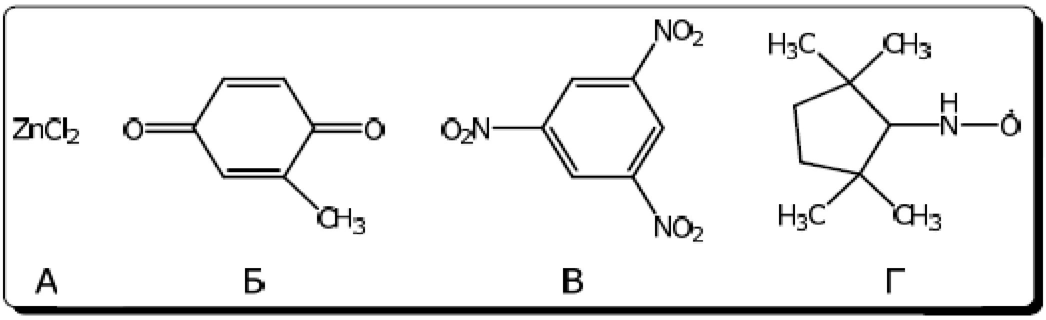


1. Formula A 2. Formula B 3. Formula C 4. Formula D

3. Preparation methods and structure of the main types of polymers

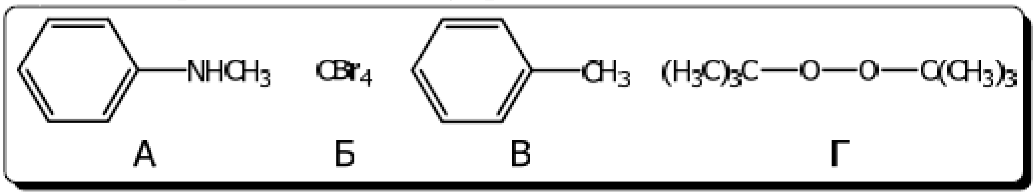
3.1. Types of polymerization. Initiation and inhibition of polymerization

1. Of the listed compounds, it does not slow down the radical polymerization of methyl methacrylate:



1. A 2. B 3. C 4. D

2.Of the substances shown in the figure, it increases the rate of polymerization of styrene in the presence of benzoyl peroxide at 20°C:



1. A 2. B 3. C 4. D

3. Polymethyl methacrylate polymerization of methyl methacrylate can be obtained in the presence of initiators:
1. benzoyl peroxide 2. n-butyllithium 3. atmospheric oxygen when heated to 100°C 4. aluminum oxide

4. Syndiotactic head-tail polymethyl methacrylate can be obtained from methyl methacrylate by heating in benzene solution at 70°C in the presence of cumene hydroperoxide

1. γ-irradiation in bulk at 58°C
2. polymerization in a solution of tetrahydrofuran in the presence of butyllithium at -78°C
3. UV - irradiation in bulk at -70°C in the presence of azobisisobutyronitrile
4. polymerization in toluene in the presence of butyllithium at -78°C

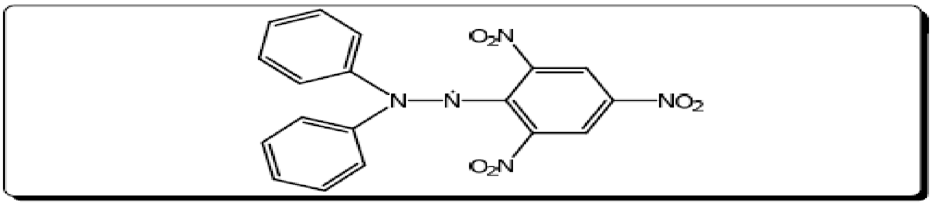
5. Polymerization of styrene is caused by:

1. potassium-naphthalene complex 2. ammonium persulfate 3. sodium chloride
4. isopropylbenzene hydroperoxide 5. trichloroacetic acid 6. diethylmagnesium
7. triisobutylaluminum vanadium (III) chloride

6. By the mechanism of "living chains" in the presence of butyllithium polymerizes: 1. isobutylene 2. styrene 3. vinyl butyl ether 4. propylene

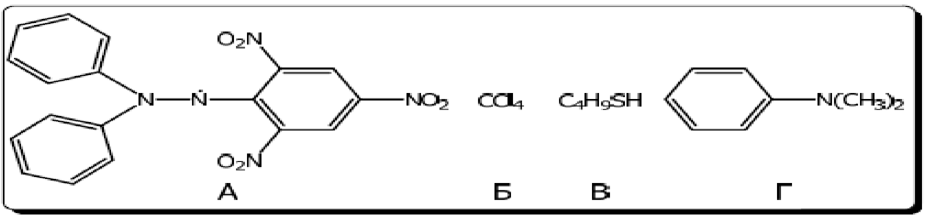
7. Under the action of catalysts based on Lewis acids will polymerize:
1. isobutylene 2. acrylonitrile 3. methyl methacrylate

8. The addition of diphenylpicrylhydrazyl to the vinyl acetate-benzoyl peroxide system, which polymerizes at 80°C, leads to:

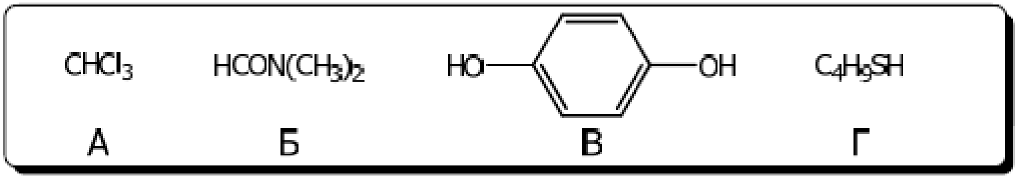


1. reaction inhibition (complete suppression of polymerization) 2. polymerization slowdown
3. accelerate polymerization 4. decrease the degree of polymerization without affecting the polymerization rate

9. Of the substances shown in the figure, it inhibits (completely suppresses) the polymerization of vinyl acetate initiated by benzoyl peroxide:



1. A 2. B 3. C 4. D
10. Of the substances shown in the figure, it inhibits (completely suppresses) the polymerization of acrylic
lonitrile initiated by the decomposition of azobisisobutyric acid dinitrile at 60°C



1. A 2. B 3. C 4. D

eleven. High molecular weight atactic polymethyl methacrylate can be obtained from methyl methacrylate:
1. UV - irradiation in bulk at -70°C in the presence of azobisisobutyronitrile;
2. heating in a benzene solution at 70°C in the presence of acetyl peroxide;

3. polymerization in a solution of toluene at -70°C in the presence of butyllithium;
4. UV - irradiation in bulk at 40°C in the presence of azobisisobutyronitrile;
5. heating in bulk at 60°C in the presence of diazoaminobenzene.

12. Polybutadiene, obtained by radical polymerization at 50°C, consists of a sequence of units attached according to the type:
1.1,4-cis
2. 1, 4-cis + 1, 4-trans + 1, 2
3. 1, 4-trans
4. 1, 4-cis + 1, 2

13. The highest growth rate constant during radical polymerization (under the same conditions) has:
1. vinyl chloride 2. vinyl acetate 3. methyl methacrylate 4. acrylonitrile

14. The active center of the polymerization of vinyl monomers initiated by the "iron (II) cation + hydrogen peroxide" system is:
1. free radical 2. no polymerization 3. cation 4. anion

15. Polymerization of styrene in water in the presence of charged particles of potassium cation and sulfate radical anion proceeds according to:
1. anionic mechanism 2. cationic mechanism 3. radical mechanism
4. polymerization does not occur
16. Water can serve as a cocatalyst in polymerization:
1. initiated by butyllithium 2. initiated by boron fluoride
3. in a solution initiated by benzoyl peroxide
4. in an emulsion initiated with potassium persulfate

17. Polymerization of vinyl butyl ether is caused by:
1. lithium in toluene 2. tin (IV) chloride in benzene 3. lithium in tetrahydrofuran
4. sodium in ammonia

18. Organometallic compounds of alkali metals initiate polymerization:
1. ethylene oxide 2. vinyl butyl ether 3. isobutylene

19. Stereoregular isoactic polypropylene can be obtained from propylene:
1. high pressure radical polymerization
2. coordination ion polymerization on complex organometallic catalysts
3. anionic polymerization by the method of "living chains"
4. Cationic polymerization at low temperature

3.2. Thermodynamics of polymerization

1. The ratio of constants of iso- and syndio-additions in the radical polymerization of methyl methacrylate

in solution determines:
1. concentration of the monomer in the solvent
2. type and concentration of initiator
3. curing temperature

2. For the kinetic derivation of the expression for the polymerization-depolymerization equilibrium constant in the form K=1/[M], [M] is the equilibrium monomer concentration, the following assumptions are used:
1. condition of quasi-stationarity
2. independence of the reactivity of the active center of macromolecules from the chain length
3. equality of chain growth and chain termination rates
4. formation of a polymer with an average degree of polymerization >>1

3. A solution of alpha-methylstyrene in benzene with a concentration of 5.0 mol/l was prepared for polymerization. The concentration of the resulting polymer (per mol of link) after the establishment of polymerization-depolymerization equilibrium in the system at 20°Sudlanowchi (Kravnov at 20°C is 0.45 l/mol) is in the range of values:
1. 2.0 - 3.0 2. 1.0 - 2.0 3. 0.1 - 1.0 4. 0.01 - 0.1

4. The depth of transformation in the reaction mixture as a result of the polymerization reaction at a temperature of 27 ° Sudlanowchi (the initial concentration of the monomer was 1 mol / l, the change in standard entropy was -25 cal / (mol deg), and the thermal effect of the reaction was 10.26 kcal / mol) is equal to:
1. 50% 2. 15% 3. 99% 4. 0%

5. To describe the constant of polymerization-depolymerization equilibrium from the above relations, it is true:

1. $K_{равн} = [M]_{равн} \cdot e^{-\Delta Q_{пм}/RT}$
2. $K_{равн} = RT \cdot Ln\left([M]_{равн} + \frac{1}{\bar{\bar{P}}_N}\right)$
3. $K_{равн} = \frac{1}{[M]_{равн}}$
4. $K_{равн} = RT \cdot Ln[M]_{равн}$

6. The equilibrium yield of the polymer after the polymerization of methyl methacrylate at 260°C (change in standard entropy -125.5 J/(mol deg), thermal effect of the reaction 62.8 kJ/mol, and initial monomer concentration 1 mol/l) is equal to:
1. 0% 2. 10% 3. 50% 4. 100%

7. The activation energy of radiation-chemical initiation of radical polymerization is equal to:
1. +40 kJ/mol 2. 0 kJ/mol 3. +120 kJ/mol 4. -20 kJ/mol

8. The value of the activation energy E (kJ / mol) of photochemical initiation is within:
1. 0 ≤ E ≤ 10 2. 10 ≤ E ≤ 20 3. 40 ≤ E ≤ 80 4. 80 ≤ E ≤ 120

9. If polymerization is characterized by an increase in entropy, then disclosure occurs:
1. C=C bonds 2. unstrained cycles 3. such polymerization is impossible 4. C=O bonds

10. The critical polymerization temperature of the TKR of a certain monomer (the thermal effect of its polymerization is 54 kJ/mol, and the entropy of polymerization is -100 J/mol deg) is within the limits (values are given in kelvins):
1. 300 to 400 2. 400 to 600 3. 200 to 300 4. 100 to 200
11. The existence of an upper or lower limiting temperature for the polymerization of monomers is determined by:
1. the sign of the entropy of polymerization 2. the sign of the enthalpy of polymerization
3. ratio of signs of enthalpy and entropy of polymerization
4. is determined only by the ratio of the absolute values of enthalpy and entropy

12. Necessary and sufficient for systems characterized by the upper limiting temperature of polymerization (DH (0) and DS (0) - changes in the standard enthalpy and entropy of polymerization), is the condition:
1. DH(0)<0, DS(0)<0 2. DH(0)<0, DS(0)>0 3. DH(0)<0 4. DH(0)>0

13. Necessary and sufficient for systems characterized by the lower limiting temperature of polymerization (DH(0) and DS(0) - changes in the standard enthalpy and entropy of polymerization) is the condition:
1. DH(0)>0 2. DH(0)=0, DS(0)>0 3. DH(0)<0, DS(0)<0 4. DH(0)<0, DS(0)>0

3.3. Basic equation of radical polymerization

1. The order of the reaction of adding methyl methacrylate to the end of the growing chain at the initiator during its oligomerization in the presence of a sufficiently large amount of benzoquinone is:
1.1.5 2.1.0 3.0.0 4.0.5

2.Maximum number average molecular weight of MN in the polymerization of methyl methacrylate at 50°C, with photochemical initiation (growth rate constant KP=410 l/(mol s), termination rate constant KO=24 106 l/(mol s), concentration monomer M=9.25 mol/l, the rate constant of chain transfer to the monomer KM=1.95 l/(mol sec), polymerization rate V(PM)=1 10-5 mol/(l sec)) is in the range of values:
1. 104 < MN ≤ 106 2. 106 < MN ≤ 108 3. 10 < MN ≤ 102 4. 102 < MN ≤ 104

3. For the order of radical polymerization according to the concentration of the initiator (II) in the presence of two types of chain termination reactions simultaneously in the polymerization system: 1) on weak inhibitor molecules and 2) quadratic termination as a result of recombination of propagating radicals, the following expression is correct:
1. P=1 2. $0.5 < P < 1$ 3. P=0 4. $0 < P < 0.5$

General issues

1. Questions for educational discussion No. 1 "Synthesis of polymers".

1. Determine the type of mechanism for initiating the polymerization reaction from the values of the activation energy of the stages of chain growth and termination.
2. Calculate the number average molecular weight of the polymer according to the given values of the growth constants, the rate of chain termination and transfer to the monomer.
3. Calculate the length of the macromolecular chain from the given values of the rates of chain growth and termination.
4. Calculate the rate constant of initiation at given concentrations of the monomer and initiator from the rate of initiation.
5. Indicate the necessary thermodynamic conditions for the existence of the upper and lower limiting polymerization temperatures.
6. Assess the dependence of the ratio of the probabilities of linear polycondensation and cyclization for amino acids on the length of the radical separating the carboxyl and amine groups.
7. Calculate the initial ratios of the components of the polycondensation reaction according to the given value of the gelation point.
8. Calculate the maximum possible degree of polymerization in the polycondensation reaction according to the given initial amounts of monomers.
9. Calculate the initial amounts of reagents required to obtain a polycondensation polymer with a given degree of polymerization.
10. Estimate the relative tendency of a number of monomers to alternate with methyl methacrylate in radical copolymerization.
11. Indicate the likely type of copolymer for a given pair of monomers under known conditions.
12. Determine the composition of the copolymer by the values of copolymerization constants.
13. Indicate the nature of the influence of temperature on the degree of polymerization of a cyclic monomer under given conditions.
14. Evaluate the composition of a copolymer made from known monomers by anionic/cationic polymerization.
15. Determine the nature of the influence of the nature of the solvent on the rate of polymerization.
16. Calculate the equivalence coefficient for a given mixture of monomers.
17. Determine the most effective initiator for the polymerization of some monomer.
18. Determine the structure of the active center in the polymerization reaction.

2. Questions for educational discussion No. 2 "Chemical properties and chemical transformations of polymers."

1. Estimate the probability of obtaining a monomeric product during thermal degradation of polymers.

2. Determine the configurational structure of the polymer chain by the chemical composition of the degradation products.
3. Specify the most efficient way to obtain a block copolymer of a given composition.
4. Indicate the characteristic patterns of the process of chemical transformation of the polymer.
5. By the form of the kinetic curve of the hydrolysis of the stereoregular polyester, determine the nature of the distribution of links in the hydrolysis products.
6. Estimate the relationship between the glass transition temperatures of the graft copolymer and its individual components.
7. Determine the chemical composition of the polymer degradation products.
8. Determine the most effective stabilizer for the process of thermal-oxidative degradation of the polymer.
9. Based on the kinetics of the hydrocarbon polymer chlorination reaction, evaluate the nature of the distribution of substituted positions along the chain.
10. Indicate polymers that form intramolecular cycles during pyrolysis while maintaining their polymeric nature.
11. Indicate methods to distinguish a mixture of homopolymers from a graft copolymer.

3. Questions for educational discussion No. 3 "Macromolecules in Solutions".

1. Characterize the dependence of the lower critical temperature of polymer dissolution on its molecular weight.
2. Characterize the change in the second virial coefficient with a change in temperature in the LCTE–UCTE range for a given ratio between critical temperatures.
3. Estimate the value of the relative decrease in the elasticity of the solvent vapor over the polymer solution from the given value of the free energy of mixing the polymer–solvent.
4. Evaluate the nature of the geometric shape of macromolecules according to the given values of molecular weight, Mark-Kuhn-Houwink constant and intrinsic viscosity.
5. Characterize the dependence of the intrinsic viscosity of a polymer solution with LCST (UCST) on temperature.
6. Characterize the change in the reduced viscosity of the polyelectrolyte solution with a change in the ionic strength of the solution.
7. Characterize the change in the parameters of the Mark-Kuhn-Houwink equation with a change in the chemical nature of the solvent.
8. Describe the dependence of the degree of swelling of polyelectrolytes on the pH value.
9. Indicate the nature of the relationship between the root-mean-square distance between the ends of the chain of macromolecules and the intrinsic viscosity of the solution.

10. Characterize the change in the intrinsic viscosity of the polymer solution when a precipitant is added.
11. Determine the direction of movement of protein macromolecules under given conditions.
12. Characterize the form of curves of potentiometric titration of polyelectrolyte.
13. Characterize the change in the pH of the polyelectrolyte solution when low molecular weight electrolytes are added.
14. Characterize the dependence of the second virial coefficient in a mixture of two solvents on the composition of the mixture.
15. Estimate the ratio between the viscometric molecular weights of the polymer, determined from the viscometric data of the solution in good and poor solvents.
16. Specify the conditions that make it possible to measure the molecular weight of polyelectrolytes by the osmometric method.
17. Characterize the effect of pH on the specific viscosity of polyelectrolyte solutions.

4. Questions for educational discussion No. 4 "Polymer bodies".

1. Estimate the elasticity modulus of the cross-linked polymer by the value of the equilibrium degree of swelling.
2. Compare the values of residual deformation of polymers with different structures.
3. Estimate the melting temperature of the polymer according to the given values of the thermodynamic parameters of the melting process.
4. Indicate the nature of the dependence of the elasticity of the polymer body on temperature for ideal and non-ideal elastomers.
5. Characterize the type of X-ray diffraction pattern for a stretched sample of a crystalline polymer.
6. Characterize the nature of the temperature dependence of the deformation of a polymer sample under a constant load.
7. Estimate the glass transition temperature of the crosslinked polymer from the degree of crosslinking and the value of the mechanical segment.
8. Characterize the temperature dependence of the glass transition temperature for amorphous polymers.
9. Calculate the durability of a loaded polymer sample under given conditions.
10. Specify the relative values of the glass transition temperature for polymers of known chemical composition.
11. To characterize the influence of the cooling rate of the molten amorphous polymer on the density of the glassy polymer matrix.
12. Characterize the change in the interval between the glass transition and flow temperatures with an increase in the molecular weight of the polymer.

5. Questions for self-control

1. Definition and operational properties of polymers.
2. Nomenclature and classification of polymers by chemical structure and method of preparation. Physical and chemical properties of polymers.

3.Average molecular weights. Methods for determining the average number average, weight average and viscosity average molecular weight.
4. Size, shape and flexibility of the macromolecule.Definitions of a macromolecule, configuration, conformation.
5. Mechanisms of flexibility, kinetic and thermodynamic flexibility.
6. Model of a free-jointed chain. Fixed angle model. The effect of retarded rotation.
7. General ideal expression of dependence of root-mean-square distance between chain ends on chain length, Kuhn's segment.
8. Worm-shaped (persistent) model of a rigid polymer chain. The effect of long-range interactions on the shape of flexible chains, the excluded volume effect, and the Flory linear expansion parameter.
9. Dilute solutions of polymers.Features of the dissolution of polymers.
10. Statistical calculation of thermodynamic functions, lattice models, theory of strictly regular solutions, enthalpy of mixing, Hildebrand solubility parameters.
11. Free energy of mixing of real solutions. Deviation of the behavior of polymer solutions from the behavior of ideal solutions.
12. Flory-Hagins theory of polymer solutions.
13. Critical phenomena in polymer solutions, solution stability, solubility diagrams, θ-state.
14. Phase diagrams. Colligative properties of solutions, osmotic pressure.
15. Hydrodynamic properties of solutions. Einstein's equation for the viscosity of a suspension of hard balls. Huggins equation for polymer solutions. Relationship between viscosity and size of polymer coils, Flory-Fox equation, Flory linear expansion parameter.
16. Aggregate and phase states of polymers. Amorphous states, glassy, highly elastic and viscous. crystalline state. Liquid crystal state, thermotropic and lyotropic structures. supramolecular structures.
17. Modern aspects of describing the properties of dilute polymer solutions.Concentration boundaries between areas of dilute,
semi-dilute and concentrated solutions.
18. Unperturbed sizes of macromolecules. Flexibility of the polymer chain in the unperturbed state. Excluded volume effect.
19. Inside and intermolecular interactions. Sizes of polymer coils in good, theta and bad solvents.
20. Polyelectrolytes, expansion and collapse of coils, Manning's theory of condensation of counterions.
21. Concentrated solutions and melts of polymers.
22. Rheology: definition, simple rheological equations.
23. Newtonian and non-Newtonian fluids. Features of the flow of pseudoplastic anomalously viscous liquids.
24. Influence of temperature, polymer concentration, thermodynamic quality of the solvent, molecular weight, branching and polydispersity of macromolecules on the viscosity of concentrated solutions and polymer melts.
25. Methods for studying the physical properties of polymers.

26. Gaussian distribution of vectors between the ends of a chain for an ideal chain.

27. High elasticity of polymer networks: property of high elasticity, elasticity of a separate ideal chain, elasticity of polymer networks.

28. Methods for describing mechanical properties, basics of rheology: elastic behavior, viscous behavior, Maxwell model, Kelvin-Voigt model, Burger model and deformation behavior of polymeric materials.

29. Physical and chemical bases of polymer synthesis.

30. Polymerization, definition, classification, basic properties. radical polymerization. anionic polymerization. cationic polymerization. Copolymerization.

31. Chemical transformations of polymers.

32. Polycondensation, definition, classification, monomers, main and side reactions, kinetics, catalysis, molecular weight distribution, copolycondensation.

33. Polymer-analogous transformations.

34. Destruction of polymers.

35. Methods for obtaining and processing polymers into products:compounding, calendering, mold casting, rotational casting, film casting, injection molding, blow molding, extrusion, thermoplastic sheet molding, foaming, reinforcement, fiber spinning.

6. Sample Questions for Exam Preparation

1. On what grounds is the nomenclature and classification of polymers based?
2. What are the main physical and chemical properties of macromolecules?
3. How can you determine the number average molecular weight?
4. What methods are used to determine the weight average molecular weight?
5. What is the mechanism of flexibility of macromolecules?
6. How does the RMS distance between the ends of the chain depend on the number of segments or the length of the chain?
7. What is the essence of the Flory-Huggins theory of polymer solutions?
8. What are the colligative properties of dilute polymer solutions?
9. What determines the hydrodynamic properties of polymer solutions?
10. What is the difference between aggregate and phase states?
11. What phase states can an amorphous polymer be in?
12. What are the main conditions for the crystallization of polymers?
13. What monomers enter into the reaction of radical polymerization?
14. What is the peculiarity of the polycondensation reaction?
15. What technological methods are used in the processing of polymers?

Collection of tasks and assignments

1. Write the reaction equations for the production of polyvinyl chloride, having calcium carbide, water, sodium chloride, sulfuric acid.

2. Write the reaction equations corresponding to the schemes:

a) CH4 ------ (- CH2- CH -)n b) C3H8 ---- (- CH2 - CH -)n
| |
ClCH3

c) C2H5OH--- (- CH2 – CH= CH- CH2-)n Specify the conditions for their occurrence.

3. In appearance, the nitron fiber is more similar to wool than others, it is quite durable and retains heat well. Nitron is obtained by polymerization of acrylic acid nitrile H2C = CH - C = N. Make a scheme for obtaining this fiber and indicate the structural unit of the resulting polymer.

4. Write the reaction equation for the copolymerization of 1,3-butadiene with methacrylic acid H2C=C(CH3)-COOH.

5. Nylon polyamide fiber is obtained by the polycondensation reaction of hexamethylenediamine
H2N - (CH2)6 -NH2 and adipic acid HOOC- (CH2)4 - COOH. Draw up a scheme for obtaining this fiber and indicate the structural unit of the resulting polymer.

6. Enanth polyamide fiber, which differs from capron in greater resistance to acids and alkalis, is obtained by the polycondensation reaction of aminoenanthic acid
H2N-(CH2)6-COOH. Draw up a scheme for obtaining this fiber and indicate the structural unit of the resulting polymer.

7. Indicate the signs by which thermosetting polymers can be distinguished from thermoplastic ones. Name all the thermosetting and thermoplastic polymers known to you. Write the equation for the chemical reaction of obtaining the thermoplastic polymer you have given.

8. High density polyethylene has a relative molecular weight of 45000, and low pressure polyethylene -300000. Determine the degree of polymerization of polyethylene (1607; 10714).

9. Polystyrene dissolves well in non-polar organic solvents: benzene, toluene, xylene, carbon tetrachloride. Calculate the mass fraction (%) of polystyrene in a solution obtained by dissolving 25 g of polystyrene in benzene weighing 85 g. (22.73%)

10. Polymerization of chloroprene produces chloroprene rubber, which is highly resistant to light, heat and solvents. Find the molecular formula of chloroprene if it is known that the mass fractions of the elements in it are:
a) carbon -54.24%; b) hydrogen - 5.65%; c) chlorine - 40.11%, and its hydrogen vapor density is 44.25. Write the reaction equation for the polymerization of chloroprene and indicate the structural unit of the resulting polymer. (C4H5CL)

11. Isoprene (2-methylbutadiene-1,3) is obtained by dehydrogenation of 2-methylbutane. Calculate the mass of isoprene that can be obtained from 420 kg of 2-methylbutane, the mass fraction of impurities in which is 12%, and the mass fraction of isoprene yield is 85%. Write the reaction equation for the polymerization of isoprene and indicate the structural unit of the resulting polymer. (296.7 kg)

12. As a monomer for the production of polymer electrical insulating coatings, a gas containing 85.7% carbon and 14.3% hydrogen is used. The relative density of the gas with respect to hydrogen is 21. Find the molecular formula of the gas, write the equation for its polymerization reaction and indicate the structural unit of the resulting polymer. (C3H6)

Chains of transformations:

1. C2H5OH ──▶C2H4──▶C2H5Br ──▶C4H8──▶CH3- CH – CH3──▶
H2C= C – CH3──▶
| |
CH3 CH3
──▶ polymer
2. C ──▶CH4 ──▶C2H2 ──▶C2H4 ──▶polyethylene
\
dimer ──▶ polymer
3. C2H6 ──▶C2H4──▶C2H6 ──▶C3H8 ──▶C3H6 ──▶polymer
4. CH4 ──▶C2H6 ──▶C2H4 ──▶C2H2──▶A──▶B──▶polymer
Set formulas A and B and name them.

7. The raw material of chloroprene rubber is acetylene. The reaction proceeds according to the scheme: acetylene─▶vinylacetylene─▶chloroprene─▶polymer of chloroprene. Write the equation for chloroprene rubber

8. Butadiene - styrene rubber is obtained by copolymerization of butadiene with styrene. Write an equation for this chemical reaction.

9. One type of butyl rubber is obtained by copolymerization of isobutylene and 2-3% isoprene in the presence of aluminum chloride. Draw an approximate scheme for the formation of butyl rubber.

10. Vulcanization of rubber is associated with the reaction of the interaction of sulfur with rubber molecules. Give the reaction scheme for the interaction of sulfur with natural and butadiene rubbers.

Synthetic macromolecular substances and polymeric materials based on them

1. Describe the properties of polymers that determine their use in the national economy.

2. What properties of polyethylene are used in its processing: a) processing into products; b) application?

3. What devices and principles of production are used in the factory for the production of polyethylene? Do they have common features with other chemical industries?

4. Polyethylene can be in the form of liquid, powder and film. How can this be explained? Where is polyethylene used?

5. Which of the following basic scientific principles of chemical production are used in the production of synthetic rubber: countercurrent, heat exchange, increase in the surface of reactants, use of a catalyst, circulation, process control?

6. Describe the methods of production of synthetic fiber and the arrangement of the main apparatus at the plant. What are the working professions of chemists at the plant?

GLOSSARY

Linear polymers -molecules, which are chemically unrelated single chains of monomer units.

Swelling- the process of penetration of a solvent into a polymer substance, accompanied by an increase in the volume and mass of the sample

Oligomers are polymers with a low degree of polymerization

Adhesion- interfacial interaction, or interaction between the surfaces of condensed bodies of different nature brought into contact (sticking).

High polymers are polymers with a high degree of polymerization.

Degree of polymerization -this is the number of links in the chain and is denoted by the letter n.

Initiators- substances in which the energy of activation of the appearance of free radicals is much less than that of the substances themselves undergoing polymerization.

cohesion- determines the relationship between molecules inside the body and within the same phase, characterizes the strength of condensed bodies and their ability to resist external force.

coacervatus- thermodynamically non-equilibrium system, similar in properties to emulsions

wetting- this is a surface phenomenon consisting in the interaction of a liquid with a solid or other liquid body in the presence of contact of three non-wettable phases, one of which is air.

Specific viscosity- shows how much the viscosity of the HWC solution has increased compared to the viscosity of the solvent.

Reduced viscosity- the ratio of specific viscosity to concentration.

salting out- phenomena in solutions of low molecular weight substances. For example, when potash is introduced into a water-alcohol solution, a homogeneous system is divided into two liquid layers.

Zoli- highly dispersed systems, they are also called colloidal solutions. Depending on the dispersion medium, they are divided into hydrosols (water) and organosols (organic medium).

Suspensions- medium and coarse systems.

Pastes- concentrated suspensions or sediment, which is formed when the suspension loses its sedimentation stability.

Peptization -the reverse process of coagulation - the disintegration of aggregates to primary particles.

thermoset- these are polymers that change irreversibly under the influence of temperature, passing from a linear structure to a network structure due to the cross-linking of filamentous molecules by bridges from the -CH2- groups (for example, the formation of rubber). These polymers have high strength and lower solubility in organic solvents compared to linear ones; they cannot be recycled.

thermoplastic- these are polymers that, when exposed to elevated temperatures, can turn into a viscous state, and after removing the temperature effect, return to their original state without chemical destruction, so their reuse is possible.

FlexibilityIt is caused by vibrations of individual parts of the macromolecule along the valence bonds –C–C–, along the angle and along the length of the bond.

Elasticitydue to vibrations of the entire polymer chain (its elongation and contraction), that is, a change in the pitch of the helix.

Plasticdue to the displacement of individual macromolecules relative to each other.

Polymerization- a chain process going through the attachment mechanism; polycondensation is a stepwise process that follows a substitution mechanism; intermediate products at individual stages can be isolated and characterized.

Polycondensation- a multi-stage process, each stage of which is an independent reaction of the interaction of functional groups.

Recombination is the combination of growing macroradicals with each other to form a covalent bond**.**

Disproportionation - the transformation of macroradicals into inactive polymer molecules as a result of intermolecular rearrangement, the transfer of an H atom from one radical to another.

Chain transfer occurs when active centers or growing radicals interact with a monomer, polymer, impurities, etc.