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FEATURES OF CATIONIC PECTIN SYNTHESIS AND PROPERTIES

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Abstract: Many polymer compounds carrying ionogenic functional groups in monomer units are used in various fields of practical activity. Due to their ability to ionize in solutions, such polymers exhibit pronounced polyelectrolyte properties, which determines their high reactivity and unique properties. This allows them to be used in medicine and the pharmaceutical industry. Among ionogenic polymers, specific properties are exhibited by polymer compounds that carry a positive charge. For obtaining polycations, polysaccharides are a promising raw material. In particular, cationic modifications allow polysaccharides to improve their interaction with biological structures and increase their solubility in water. Such modifications also make it possible to regulate the physico-chemical and biological properties of the resulting polymer systems. Based on this, the presented research synthesized pectin derivatives with polycationic properties. The structure and composition of the obtained compounds were studied by FTIR spectroscopy, titration, chromatography, elemental and X-ray structural analysis.

Keywords: polymers, polycations, modification, synthesis, pectin, oxidation, polyaldehydepectin, analysis, structure.

Introduction. A unique feature of the physicochemical, mechanical, and technological properties of macromolecular systems is that they began to be widely used to create new polymer compounds [1-3]. Unlike low molecular weight compounds, polymers obtained synthetically or isolated from natural sources exhibit a number of specific properties due to their high molecular weight, macromolecular structure, and the presence of various functional groups in the chain. The rapid development of polymer science has made it possible to design macromolecular systems with controlled structure and functionality. Such materials are widely used in medicine, biotechnology, environmental protection, and advanced technological processes. In particular, functional polymers with reactive or charged groups attract considerable attention due to their ability to interact with biological systems and various low-molecular-weight compounds.

Among the wide variety of polymers, high-molecular-weight compounds occupy a special place, in the structure of which ionogenic functional groups are present, which determine the specific properties of the resulting polymer materials. The presence of similar ionogenic groups in the macromolecule largely determines its chemical reactivity, solubility in water, biological activity, and several other characteristics. Such compounds include macromolecular systems containing cationic functional fragments in their monomer units [4-7]. Such polymers are of significant scientific and practical interest due to the possibility of directed regulation of their physicochemical, technological, and functional properties.

The growing interest of researchers in developing new methods for obtaining cationic polymers has led to the creation of a large number of materials that have found

applications in medicine, the pharmaceutical industry, the textile industry, and other areas of chemical technology. Currently, the production of polycations is carried out mainly by two main methods. The first method is based on conducting polycondensation or copolymerization reactions of the corresponding monomers. The second approach involves the chemical modification of existing polymer chains by introducing amino groups into their structure.

The peculiarity of the first synthesis method is that the change in the initial chemical structure during chemical modification allows for the purposeful regulation of the characteristics of the high-molecular-weight compound, such as the average molecular weight of the polymer chain, structure, solubility in water, as well as the reactivity and physicochemical properties of the resulting polymer. Furthermore, this approach allows for the introduction of various functional groups into the macromolecule, which contributes to the expansion of the practical applications of the synthesized materials.

An important feature of this approach is the possibility of designing polymer chains with predetermined functional groups. By selecting suitable monomers, it becomes possible to influence not only the composition but also the architecture of the macromolecule. This makes it possible to obtain polymers with linear, branched, or cross-linked structures. As a result, the physicochemical behavior of the resulting materials can be precisely controlled. Such control is especially important when polymers are intended for biomedical or technological applications.

The second approach to chemical synthesis is based on selecting a ready-made polymer base, into the structure of which positively charged functional groups are immobilized after chemical modification. In this aspect of the synthesis, the cationic groups chemically bonded to the macromolecular chain act as active centers, determining the physicochemical and functional properties of the resulting polymer. The presence of such groups ensures the ability of macromolecules to effectively interact with anionic compounds, biological macromolecules, and various surfaces. The advantage of this method is the possibility of obtaining products with different molecular-mass characteristics while preserving the initial properties of the polymer matrix. The purpose of this research is to synthesize cationic derivatives of pectin.

Methodology & empirical analysis. The work used commercial citrus pectin isolated from citrus fruit skin (Sigma-Aldrich), with an esterification degree of 60% and an average molecular weight of 150±6 kDa. As a modifying reagent, carbohydrate guanidine and sodium metaperiodate (TU 6-09-02-54-74).

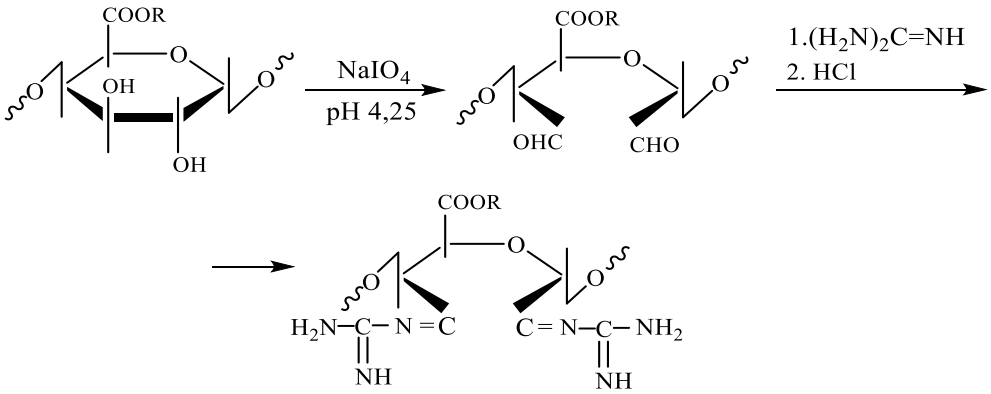
All used reagents were applied without additional purification. Distilled water was used as a solvent at all stages of synthesis and preparation of the reaction mixture. Before conducting experiments, the initial substances were stored under conditions recommended by the manufacturer, which ensured the stability of their physicochemical properties.

Periodic oxidation of pectin. To carry out the periodate oxidation reaction, 0.05 mol of pectin was placed in a 1000 ml dark glass bottle, after which 300 ml of an acetate buffer solution with a pH of 4.25 was added. The mixture was mixed until the polysaccharide

completely dissolved and a homogeneous solution was obtained. Then, a 0.5 N $NaIO_4$ solution with a pectin:IO^-=1:1 molar ratio was introduced while constantly stirring. The reaction was carried out for 2-7 hours at a temperature of 20°C under light-protective conditions, which prevented the decomposition of periodate ions. Upon completion of the reaction, the oxidation products were precipitated by adding acetone and was dried in vacuum above P_2O_5 in the dark until a constant mass. It should be noted that as a result of periodate oxidation, selective cleavage of glycol fragments of the polysaccharide chain with the formation of aldehyde groups occurs, leading to the formation of a polyaldehyde derivative of pectin (PAP). The oxidation state (r_{ox}) of the functioning pectin, determined by the reverse iodometric titration method [8], was 15-44 mol% depending on the reaction conditions and its duration.

Cationic pectin synthesis. For the synthesis of the polymer compound, an aqueous medium was used as a solvent. A pre-weighed amount of oxidized pectin (0.05 mol) with varying degrees of oxidation was placed in a 1 L reaction vessel and dissolved in 50-100 ml of distilled water while constantly stirring on a magnetic stirrer until a homogeneous solution was fully formed. After complete dissolution, guanidine carbonate solution was gradually introduced into the solution (1:2 ratio) at a controlled rate, ensuring uniform distribution of reagents and optimal conditions for the formation of azomethine bonds between the aldehyde groups of pectin and the amino groups of guanidine. The reaction mixture was kept in a stationary state until the condensation process was complete, which ensured the formation of a stable polycation. The reaction was carried out at a temperature of 20°C for 5 hours at a pH value of 8.5. Under these conditions, the aldehyde groups of polyaldehyde pectin interact with the amino groups of guanidine, forming azomethine (Shiff) bonds. Upon completion of the reaction, 0.1 M HCl solution was added to the reaction mixture, bringing the pH value to 6.0.

The resulting reaction solution was subjected to dialysis against distilled water for 48 hours to remove low molecular weight impurities and unreacted components, which ensured the purification of the macromolecular complex and stabilization of its structure for further research.



R=H, CH_3

After the completion of dialysis, the solution was subjected to sublimation drying, resulting in a modified water-soluble polymer product. It should be noted that the introduction of guanidine fragments into the structure of polyaldehyde pectin leads to the formation of a cationic polysaccharide derivative with improved physicochemical and potentially biologically active properties. The synthesis of cationic pectin derivatives proceeds according to the following scheme:

Methods of studying cationic pectin. FTIR spectra were recorded on a Vector-22 spectrometer in the 400-4000 cm^{-1} wavelength region in KBr tablets (3 mg of sample/300 mg of KBr).

The molecular-mass characteristics of the synthesized derivatives were determined by high-performance penetrating gel chromatography on an Agilent 1260 Infiniti liquid chromatograph. The nitrogen content (N,%) in the samples was determined using an Eura EA (Italy) elementary analyzer. The guanidine content in the synthesized compounds was determined by acidimetric titration.

The pKa values in the final products of the reaction were calculated as follows: 50 mg of the sample was dissolved in water, then 0.1 n of HCl was added to the resulting solution and the pH was brought to 3. After this, titration was carried out by adding aliquotas of 0.1 N NaOH solution while constantly stirring. The pH value of the solution was monitored using a pH meter (SevenCompact S220-Basic, Mettler Toledo, Germany). Surface analysis was performed using a scanning electron microscope, EVO MA10 (Zeiss, Germany).

Results. The uniqueness of polysaccharides oxidized by periodates lies in the formation of highly reactive electrophilic aldehyde groups in the polymer chain, which selectively interact with primary amines, leading to the formation of azomethine bonds (Shiff bases). This mechanism ensures the targeted chemical functioning of polysaccharides, allowing the introduction of cationic, bioactive, or polyelectrolyte fragments with a high degree of control over the structure and distribution of functional groups. Consequently, macromolecular systems with regulated physicochemical and biological properties, including solubility, molecular flexibility, adsorption activity, and biocompatibility, are formed, making them promising materials for use in pharmaceutical, biotechnological, and medical fields.

Based on these characteristics, we synthesized cationic pectin using modified pectin with varying degrees of oxidation. The results obtained based on the research are presented in the table.

The data presented in the table show that increasing the oxidation state of pectin leads to the formation of polymer compounds with a limiting content of guanidine and a degree of substitution. In this case, the increase in the degree of substitution of pectin derivatives contributes to obtaining samples with polycationic properties, as evidenced by the results of the pKa value. The decrease in the molecular weight of the reaction products is explained by the destruction of the polymer chain during chemical modification under alkaline conditions.

In the pectin FTIR spectrum, a wide absorption band is observed in the 3310 cm^{-1} region, corresponding to the valence vibrations of the OH groups. The width is due to intramolecular and intermolecular hydrogen bonds. The deformation vibration of -CH_2 groups is observed in the 1450 cm^{-1} region. The absorption band at 2930 cm^{-1} refers to the valence vibrations of C-H bonds. The absorption in the region of 1145 and 1060 cm^{-1} refers to the C-O and C-O-C bonds. A clear difference in the IR spectrum of the oxidized pectin is characterized by the appearance of peaks at 1695 and 870 cm^{-1}, which belong to the aldehyde groups and the hemiacetal form. After the covalent bonding of guanidine with oxidized pectin, an intense peak of 1610 cm^{-1} appears in the FTIR spectrum of the synthesized sample, belonging to the azomethine bonds.

Analysis of the morphological structure of cationic pectin derivatives showed that the inclusion of guanidine in the macromolecule leads to significant changes and destruction of the supramolecular structure of the polymer. The degree of these structural transformations correlates with the level of substitution of functional groups in pectin derivatives, indicating the possibility of controlled regulation of material morphology through changes in the content of cationic molecules [12].

Conclusions. Thus, in the conducted research, pectin derivatives with various physicochemical properties were synthesized. It has been established that the introduction of cationic molecules into the composition of oxidized pectin ensures the properties of polycations in the entire polymer chain. The obtained pectin derivatives can be used as polymer compounds for various purposes.

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Table 1. Main properties of synthesized pectin derivatives

№	r_{ox} PAP, mol%	Nitrogen content, %	Degree of substitution, mol%	Guanidine content, %	pKa value	$[\eta]^*$, dl/g	M^*, Da
1	15	6,0	28	7,2	8,0±0,1	0,25	30000
2	23	8,5	41	10,2	8,3±0,1	0,23	26000
3	30	10,5	56	14,0	8,5±0,1	0,18	18000
4	38	13,1	70	20,1	9,1±0,1	0,15	15000
5	44	15,0	85	23,3	9,5±0,1	0,11	12000

Note. [ɜ]* - characteristic viscosity of the samples, M-molecular mass

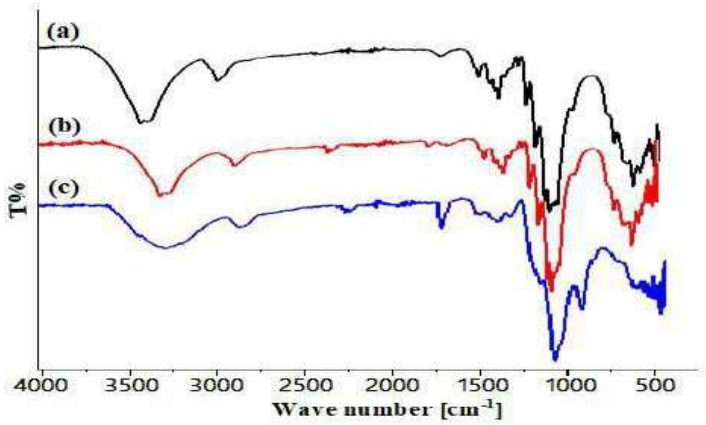

Figure.1. FTIR spectra of pectin (a), oxidized pectin (b) and cationic pectin (c)

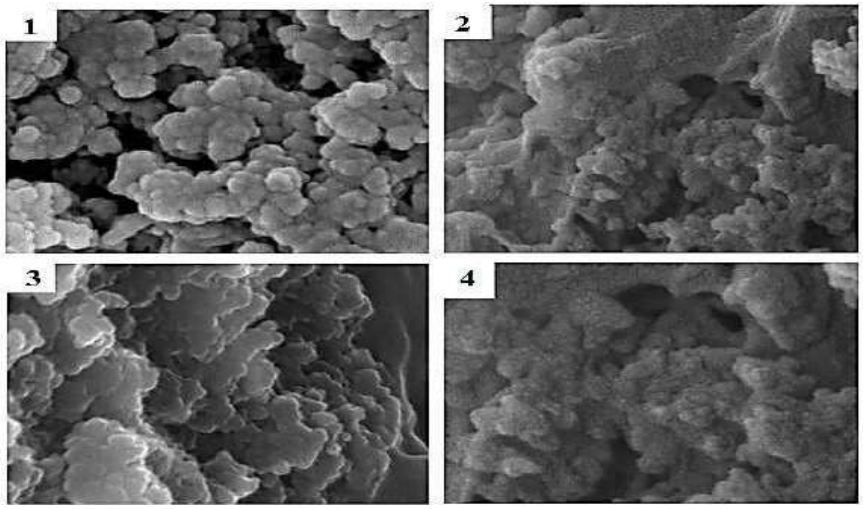

Figure 2. Electron images of pectin (1), cationic pectin with a substitution degree of 28 (2), 70 (3) and 85 (4) mol%

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