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## OXIDATION KINETICS, THERMAL PROPERTIES, AND FUNCTIONAL ACTIVITY OF CARBOXYMETHYL INULIN

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**Abstract**

This study investigates the properties of dialdehyde carboxymethyl inulin samples obtained as a result of the periodate oxidation reaction of carboxymethyl inulin. The dependence of the oxidation process on time, the effect of the degree of substitution, and the selectivity of the reaction were analyzed. Thermal analysis was conducted to examine the thermal stability of inulin and its modified derivatives, identifying the influence of structure and functional groups on degradation.
**Keywords:** *carboxymethyl inulin, periodate oxidation, dialdehyde polysaccharide, thermal analysis*

### Introduction

In recent years, extensive research has been conducted on the development of next-generation materials based on natural polymers in the fields of chemistry, chemical technology, medicine, and pharmaceuticals. Dialdehyde polysaccharides hold a special place in this area, as they are primarily obtained through the oxidation of natural polysaccharides such as cellulose, starch, chitosan, and others. These dialdehyde polysaccharides contain aldehyde groups, which provide high reactivity and modifiability. Due to their antibacterial properties, regenerative activity, and lack of toxicity, they are becoming increasingly important in polymer chemistry, medical applications, and industrial material production.

Dialdehyde polysaccharides are mainly synthesized through the selective oxidation of vicinal diol groups using sodium periodate ($NaIO_4$) or potassium periodate ($KIO_4$). The reaction depends on the structure of the polysaccharide, the concentration of the oxidizing agent, pH level, temperature, and time. For instance, dialdehyde cellulose can be obtained by oxidizing microcrystalline cellulose with 0.1–0.5 M $NaIO_4$ for 4 to

24 hours (Chang-Qing Ruan, Xiaoou Kang, Kaifang Zeng, 2022; Simona Káčerová, Monika Muchová, Hana Doudová, Lukáš Münster, Barbora Hanulíková, Kristýna Valášková, Věra Kašpárková, Ivo Kuřitka, Petr Humpolíček, Zdenka Víchová, Ondřej Vašíček, Jan Vícha Chitosan 2023; Wenjie Wang, Wen-Can Huang, Jie Zheng, Changhu Xue, Xiangzhao Mao, 2023). Similarly, dialdehyde starch is synthesized through periodate oxidation at 20–30 °C, depending on the type of starch used as the raw material (Wei Ding, Yanbei Wu, 2020; Wegrzynowska-Drzymalska K., Grebicka P., Mlynarczyk D. T., Chelminiak-Dudkiewicz D., Kaczmarek H., Goslinski T., Ziegler-Borowska M., 2020). Additionally, in dialdehyde chitosan, carbonyl groups are formed due to the cleavage of the $C_2$–$C_3$ bonds (Sherif M. A.S. Keshk, Ahmed M. Ramadan, Abdullah G. Al-Sehemi, Ahmad Irfan, Samir Bondock, 2017; Gao C., Wang S., Liu B., Yao S., Dai Y., Zhou L., Qin C., Fatehi P., 2021).

The oxidation of all polysaccharides generally leads to the opening of the polysaccharide ring, resulting in the formation of two aldehyde groups per repeating unit. This modification creates a basis for subsequent immobilization and conjugation reactions. The dialdehydation process significantly affects the molecular structure and physicochemical properties of polysaccharides. Aldehyde groups are mainly positioned at the $C_2$ and $C_3$ sites, making them highly reactive centers. The structural properties of the synthesized products, such as solubility, viscosity, and bioactivity, depend on the level of aldehyde formation, which directly contributes to the formation of stronger, covalently bonded structures between polymer chains (Tiina Nypelö, Barbara Berke, Stefan Spirk, Juho Antti Sirviö. 2020; Carolina O. Pandeirada, Max Achterweust, Hans-Gerd Janssen, Yvonne Westphal, Henk A., 2022; Xia Sun, Feng Jiang, 2024).

Dialdehyde polysaccharides are biologically active, easily modifiable, environmentally friendly, and offer broad potential applications in medicine. Their ability to form bonds with other active compounds through aldehyde groups plays a crucial role in the development of innovative materials across various fields.

## Objective of the study

The aim of this research is to study the structural and functional transformations of carboxymethyl inulin under periodate oxidation conditions and to evaluate the reactivity of the resulting dialdehyde carboxymethyl inulin, particularly its reactions with primary amine compounds.

## Materials and methods

The study utilized inulin, sodium carboxymethyl inulin (Na-CMI) with various degrees of substitution, as well as chemically pure and analytically pure reagents for experiments.

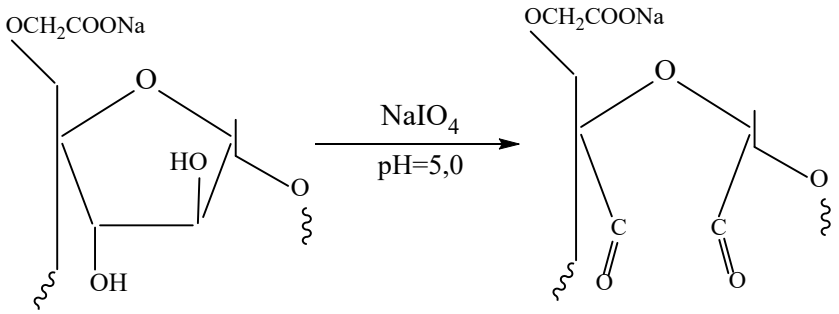
*Synthesis of Polyaldehyde Derivatives of Carboxymethyl Inulin*. A sample of carboxymethyl inulin (3 g) was measured and placed into a 500 ml heat-resistant dark glass vessel. Then, 100 ml of water was added, and the mixture was stirred on a magnetic stirrer. After dissolving the sample, 150 ml of freshly prepared acetate buffer solution with pH = = 5 was added. After thorough mixing, a 0.2 N $NaIO_4$ solution was added in a carboxymethyl inulin: $NaIO_4$ = 1:1 molar ratio. The oxidation of carboxymethyl inulin proceeded at t = 20–25 °C for 1–6 hours. To terminate the reaction, 50 ml of ethylene glycol was added. After completion of the reaction, the resulting mixture was dialyzed in distilled water until complete removal of $IO_4^-$ and $IO_3^-$ ions (monitored using silver nitrate solution). The quantitative content of aldehyde groups in the final product, dried by lyophilization, was analyzed by iodometric titration.

*Determination of Thermal Stability of Polysaccharide Samples Using TG DSC Method*. Thermo-analytical studies of the samples were carried out using a STA-409 PG TG-DSC analyzer manufactured by NETZSCH, equipped with a K-type (Low RG Silver) thermocouple and aluminum crucibles. For experiments, samples weighing 5–6 mg were used. All measurements were performed in an inert nitrogen atmosphere with a flow rate of 50 ml/min. The heating rate during measurements was 10 K/min, and the temperature range was +20...+600 °C. The measurement system was calibrated using standard substances – indium, bismuth, tin, zinc, and cesium chloride.

## Result and discussions

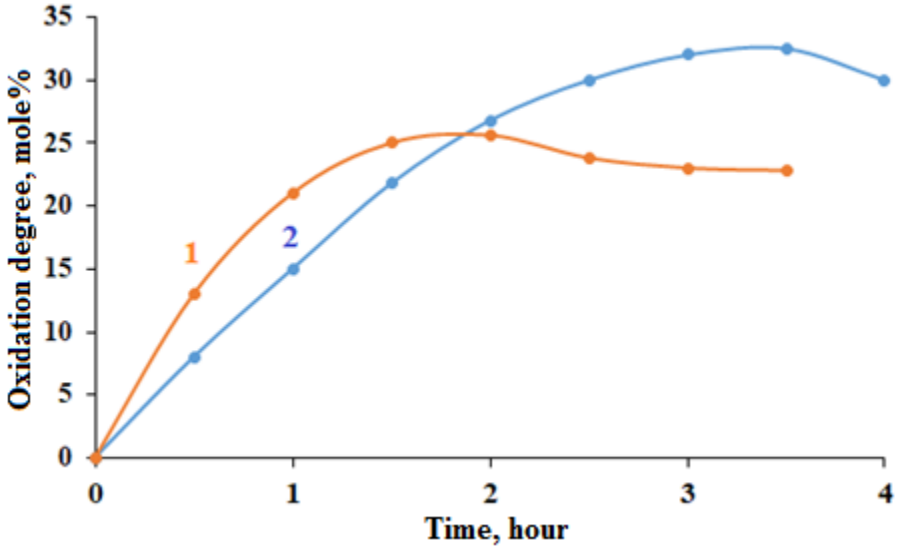
In the periodate oxidation process of polysaccharides, maintaining the selectivity of the reaction is crucial. This is because the presence of periodate ions in the reaction medium can further oxidize the formed -CHO groups to -COOH groups. As a result, the number of aldehyde groups in the synthesized dialdehyde polysaccharides decreases significantly.

The periodate oxidation reaction of carboxymethyl inulin samples at pH=5.0 was carried out according to the following scheme:




The effect of time on the oxidation degree of Na-CMI samples with different degrees of substitution was studied. The experimental results are presented in Figure 1.

**Figure 1.** *Effect of time on periodate oxidation of Na-CMI samples with substitution degrees of 85 mol% (1) and 34 mol% (2)*



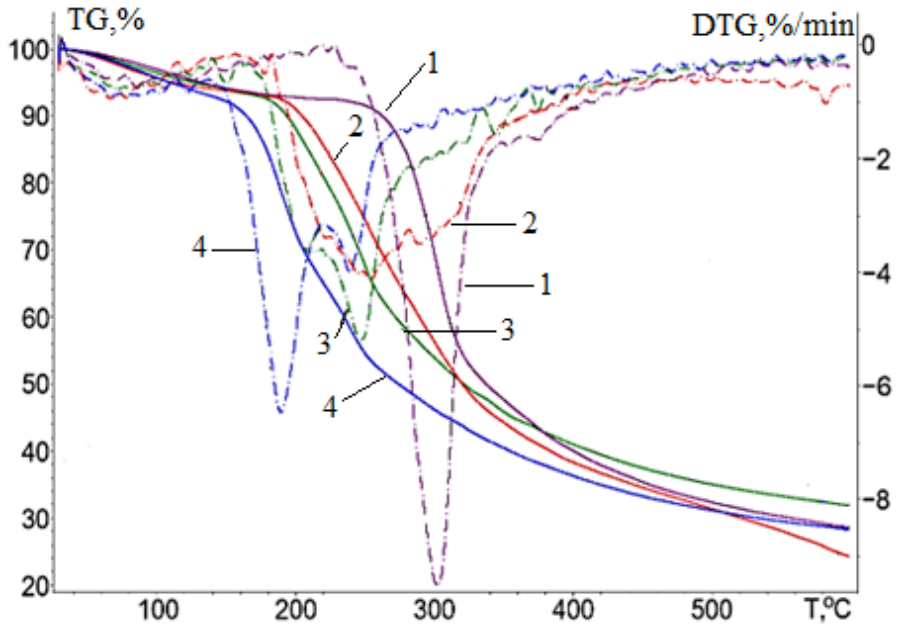

As seen from Figure 1, the oxidation degree of the Na-CMI sample with a substitution degree of 85 mol% increases from 13 mol% to 21 mol% in the first 0.5–1 hour. Extending the oxidation reaction beyond 2 hours leads to a decrease in the number of aldehyde groups from 26 mol% to 23 mol%. This is due to the oxidation of the formed aldehyde groups to -COOH by the $IO_4^-$ ions present in the reaction medium.

A sample of sodium carboxymethyl inulin (Na-CMI) with a substitution degree of 34 mol% exhibited oxidation degrees of only 8 and 14 mol% during the initial 0.5–1 hour. This slow reaction rate is attributed to the low content of hydrophilic $-CH_2-COO^-$ groups in the inulin macromolecule. However, extending the oxidation reaction to 3 hours resulted in a dialdehyde carboxymethyl inulin (DACMI) sample with an oxidation degree of 33 mol%. Oxidation of Na-CMI over 3.5 to 4 hours led to a gradual decrease in aldehyde groups.

Thermal analysis, a method for studying how substances change under the influence of temperature, was employed to investigate the thermal properties of inulin and its modified derivatives such as Na-CMI and DACMI. The objectives were to determine the thermal stability of these polysaccharides, assess the impact of substitution or oxidation degrees on their thermal properties, and evaluate their resistance for various processing

applications. The thermal characteristics of inulin, carboxymethyl inulin, and DACMI samples with varying degrees of oxidation are presented in Figure 2.

**Figure 2.** *Thermal analysis of 1-Inulin; 2-Na-CMI (substitution degree 34 mol%); 3-DACMI (oxidation degree 14 mol%); 4-DACMI (oxidation degree 33 mol%)*




As shown in Figure 2, introducing -CH2-COO⁻ or -CHO groups into the inulin macromolecule alters the polysaccharide's temperature stability and its degradation mechanism. Thermal analysis results indicate that all samples undergo degradation in three stages:

- The first stage occurs between 68–165 °C, where adsorbed moisture begins to evaporate;
- In the second stage, between 165–390 °C, the polysaccharide chain starts to degrade;
- In the third stage, at 390–600 °C, the process concludes with carbonization.

Notably, in the second stage, all samples exhibit a weight loss of approximately 48%. Differential thermogravimetric (DTG) curves reveal that the degradation of carboxymethyl inulin and DACMI samples occurs in two parts (at 190–218 °C and 230–256 °C), whereas the thermal degradation of the inulin macromolecule proceeds at around 300 °C. Additionally, the carbonization temperature of inulin derivatives is lower compared to that of inulin itself.

To confirm the presence of aldehyde groups in the Na-CMI macromolecule and determine their reactivity, we conducted a reaction with hydroxylamine, a nucleophilic reagent with high reactivity commonly used in the quantitative analysis of aldehyde groups. The reaction between DACMI and hydroxylamine was carried out according to the following scheme:

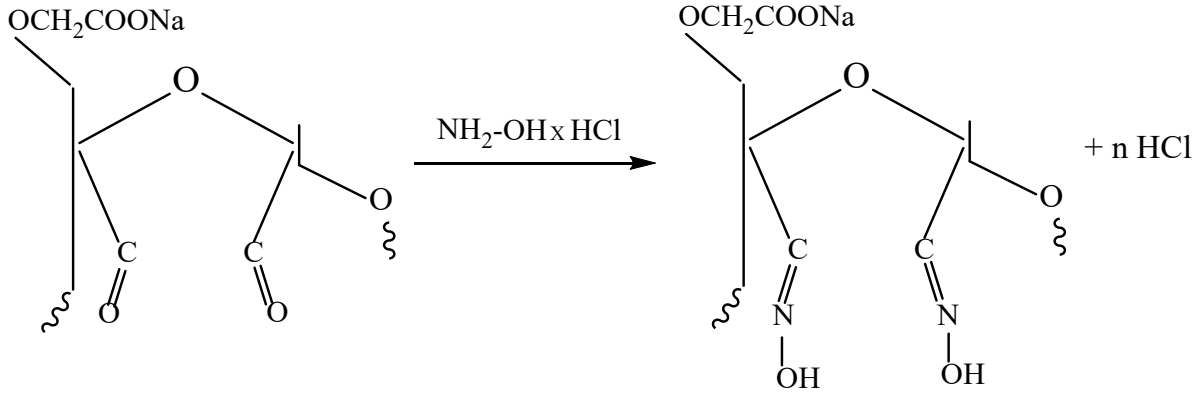


Table 1 presents the composition of compounds synthesized from DACMI samples with varying oxidation degrees and hydroxylamine. The data indicate that as the oxidation degree of DACMI samples increases, the nitrogen content in the reaction products also rises. This finding demonstrates the feasibility of chemically attaching various primary amines to the DACMI macromolecular chain, suggesting the potential application of inulin ethers as polymer matrices.

**Table 1.** *Composition of compounds synthesized from DACMI and hydroxylamine (DACMI: $NH_2$ -OH = 1:2.5; t = 20–25 °C; τ = 1 hour)*

| № | DACMI oxidation degree, mole % | Nitrogen content,% | Substitution degree, mole% |
|---|---|---|---|
| 1. | 14 | 1,1 | 12 |
| 2. | 21 | 1,8 | 19 |
| 3. | 26 | 2,1 | 25 |
| 4. | 30 | 2,5 | 29 |
| 5. | 33 | 2,8 | 33 |

The data presented in Table 1 indicates a consistent increase in nitrogen content corresponding to the rise in oxidation levels. This suggests that as the number of aldehyde groups formed through oxidation in the DAKMI molecule increases, they react with hydroxylamine to form oxime bonds. The nitrogen content serves as a direct indicator of the amount of hydroxylamine participating in this reaction.

Additionally, the formation of more functional groups leads to higher reactivity with hydroxylamine. This reactivity is directly linked to the number of reactive sites within the DACMI structure. Notably, despite the reaction between DACMI and $NH_2OH$ being conducted at 20–25 °C for only 1 hour, the sample with an oxidation degree of 33 mole% demonstrates high efficiency.

## Conclusion

The conducted research has, for the first time, identified that the rate of oxidation reaction and the quantity of aldehyde groups in carboxymethylinulin samples are influenced by the substitution degree of the synthesized polysaccharide ester and the reaction time. An increase in the oxidation degree enhances the reactivity of the DACMI molecule with hydroxylamine, providing the ability to control structural changes and functional properties of derivatives synthesized based on DACMI.

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