Chemistry

MODIFICATION OF CHITOSAN BY POLYMER-ANALOG TRANSFORMATIONS

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Modification of chitosan (Ch) with monomethylolurea has been carried out at diferent temperatures and macromolecules of Ch with different numbers of methylurea actionable functional groups were obtained. The kinetic parameters of the grafting of methylcarbamyl radical onto Ch macromolecules at different temperatures were studied and the rate constants and activation energies of above mentioned processes were determined.

***Keywords*:** polymer, chitosan, chitin, glucosamine, acetamide, modification, polymer-analog, deprotonation.

Introduction. Among natural polymers with biological activity a special place is occupied by chitosan and its functional derivatives. Chitosan (Ch) and its derivatives as biologically active compounds of applied importance were depicted in [1–5]. In order to give the Ch proper characteristics and enlarge the aspects of its application it is necessary to carry out various polymer-analog transformations based on it. Such investigations have been carried out by the authors [2, 5].

The report describes the modification of Ch having a molecular weight of about 80 *kDa*, with monomehylolurea (MMU), with the study of chain structure of modified products and kinetic parameters of their formation.

The structure of water-soluble Ch can be represented by the following structural formula:
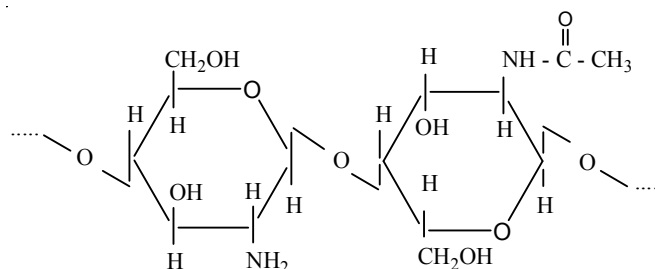

The glucosamine content in Ch on average is 92% and the acetamide content is 8%. The above presented macromolecule dissolves in aqueous solutions of

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mineral and organic acids. 2% aqueous solution of Ch prepared in 2% aqueous solution of acetic acid (pH 4.1) was used in our investigations according to description in [6]. At the indicated acidity the NH_2 group of glucosamine cycle becomes particularly protonated and only 10% of these groups remain in free form. In order to increase the content of free NH_2 groups in Ch to 47%, deprotonation of these groups was carried out with aqueous solution of 0.5 *mol* NaOH (pH 5.6) [6].

The chain structure of Ch can be represented in the following form.

n = 47%; m = 8.0% ; L = 45%.
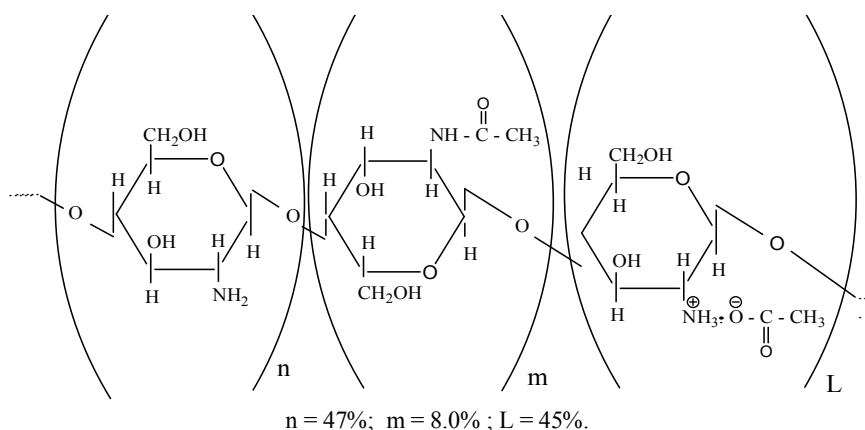
The polymer of following composition was formed modifying Ch with MMU:
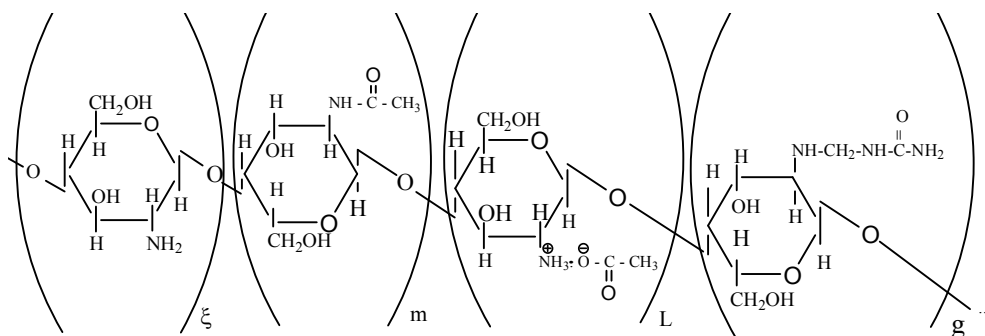
The deepness of monomer substitution depending on time and temperature is given in Tab. 1.

Using the data given in Tab. 1, the orders of condensation reaction between methylol group of MMU and amino group of Ch's glucosamine cycle were determined at different temperatures. During studies it was found that the reactions between indicated compounds can be described by the second-order rate equation [7]:

$$K = \frac{1}{t} \cdot \frac{1}{A_0 - B_0} \lg \frac{B_0(A_0 - X)}{A_0(B_0 - X)}, \qquad (1)$$

where A_0=[MMU]$_0$, B_0=[Ch]$_0$, X is the change in the initial and final concentration of reactants.

T a b l e 1

Consumption of MMU at different temperatures: $A_0=[MMU]_0= 2.2 \cdot 10^{-1} mol/L$; $B_0=[Ch]_0=6.8 \cdot 10^{-1} mol/L$

| №	Reaction time, t, min	Consumption of MMU, *mol/L*			
		338.15, *K*	343.15, *K*	348.15, *K*	353.15, *K*
1	20	$4 \cdot 10^{-3}$	$36 \cdot 10^{-3}$	$9.3 \cdot 10^{-3}$	$1.35 \cdot 10^{-2}$
2	30	–	–	$1.57 \cdot 10^{-3}$	$2.35 \cdot 10^{-2}$
3	40	$7.10 \cdot 10^{-3}$	$1.05 \cdot 10^{-2}$	–	–
4	50	–	–	$2.7 \cdot 10^{-2}$	–
5	60	–	$1.8 \cdot 10^{-2}$	–	$4.05 \cdot 10^{-2}$
6	70	$1.2 \cdot 10^{-2}$	–	–	–
7	100	$1.98 \cdot 10^{-2}$	–	–	–
8	110	–	–	$4.45 \cdot 10^{-2}$	–
9	140	$2.17 \cdot 10^{-2}$	$2.9 \cdot 10^{-2}$	$4.68 \cdot 10^{-2}$	–
10	150	–	$3.2 \cdot 10^{-2}$	–	–
11	210	–	–	–	$6.075 \cdot 10^{-2}$

The results of kinetic investigations of reaction between MMU and Ch are given in Tab. 2.

T a b l e 2

Current concentrations of MMU and Ch at different temperatures

$t,$ min	338.15, *K*				343.15, *K*				348.15, *K*				353.15, *K*			
	1*	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
20	$4 \cdot 10^{-3}$	2.16	6.4	1.87	6.0	2.14	6.2	2.8	9.0	2.11	5.9	4.3	13.5	2.06	5.45	6.8
30	–	–	–	–	–	–	–	–	15.7	2.04	5.2	8.27	23.5	1.96	4.45	13.3
40	7.0	2.13	6.1	3.3	10.5	2.09	5.75	5.1	–	–	–	–	–	–	–	–
50	–	–	–	–	–	–	–	–	27.0	1.93	4.1	16.4	–	–	–	–
60	–	–	–	–	18.0	2.02	5.0	9.7	–	–	–	–	40.5	1.79	2.75	32.0
70	12.0	2.08	5.6	5.7	–	–	–	–	–	–	–	–	–	–	–	–
100	19.8	2.0	4.82	10.7	–	–	–	–	–	–	–	–	–	–	–	–
110	–	–	–	–	–	–	–	–	44.5	1.75	2.4	35.0	–	–	–	–
140	21.7	2.0	4.6	12.4	29.7	1.9	3.8	18.7	46.8	1.72	2.1	42.0	–	–	–	–
150	–	–	–	–	32.0	1.84	3.6	19.8	–	–	–	–	–	–	–	–
210	–	–	–	–	–	–	–	–	–	–	–	–	60.75	1.59	0.7	79.0

* **1** $- 10^3 X, mol/L$; **2** $- A_0 - 10X, mol/L$; **3** $- B_0 - 10^2 X, mol/L$; **4** $- \log B_0(A_0 - X) - \log A_0(B_0 - X)$.
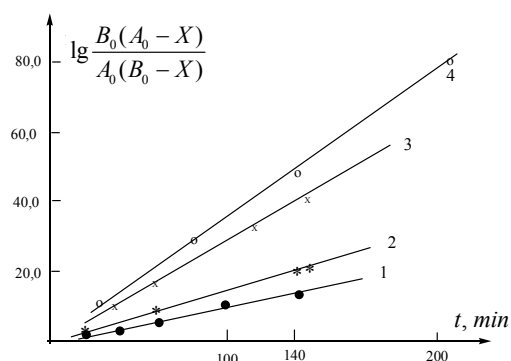
Fig. 1. Dependence $\lg \dfrac{B_0(A_0 - X)}{A_0(B_0 - X)}$ vs t at following temperatures, *K*:
1 – 338.15; 2 – 343.15; 3 – 348.15; 4 – 353.15.

In order to find the value of rate constants of interaction between MMU and Ch a plot of $\lg \dfrac{B_0(A_0 - X)}{A_0(B_0 - X)}$ vs t was constructed using the Eq. (1) and data in Tab. 2.
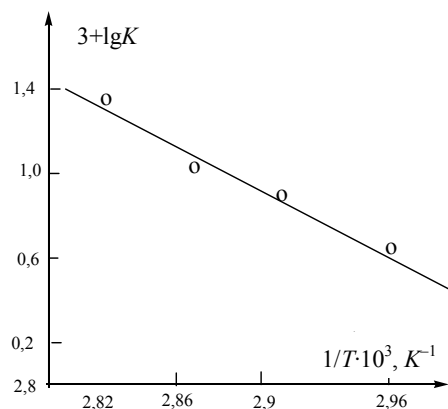
Fig. 2. lgK vs 1/T dependence.

In accordance with Fig. 1, the rate constants of the reaction between MMU and Ch were evaluated and are equal $5.8 \cdot 10^{-3}$; $8.5 \cdot 10^{-3}$; $2.04 \cdot 10^{-2}$; $2.5 \cdot 10^{-2}$ $L/(mol \cdot min)$, for 338.15; 343.15; 348.15 and 353.15 K correspondingly.

By plotting the logarithm of the rate constant K, versus the inverse temperature, $\dfrac{1}{T}$ (Fig. 2) the activation energy of the reaction between above mentioned compounds was determined $E_a = 13.8 \pm 0.1 \, kcal/mol$.

Experimental Part. Water-soluble Ch ("Bioprogress CJSC", Shelkovsk, RF) having an average molecular mass of about 80 *kDa* was used. For the preparation of 2% aqueous solution of acetic acid, glacial acetic acid ("chemically pure") was used. The content of nitrogen in initial Ch as well as after its modification was determined by the method of atomic absorption spectrophotometry (AA-3 spectrophotometer was used) and by the classical method of elemental analysis. MMU was obtained according to [8].

It should be noted that by partial protonation of $-NH_2$ group of glucosamine ring 2.38 *g* copolymer, having above mentioned chain structure, was obtained from 2 *g* initial Ch.

Conclusion. In the result of reaction of the methylol derivative of urea with chitosan it was found that the reaction order remains unchangeable at different temperatures.

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