

MODIFICATION OF CHITOSAN BY GRAFT COPOLYMERIZATION

M. L. YERITSYAN ^{1*}, A. M. ARUSTAMYAN ^{1**}, V. M. MAVISAKALYAN ^{1***},
I. N. SIREKANYAN ^{1****}, S. V. TSARUKYAN ^{2*****}

¹ Armenian State Pedagogical University after Kh. Abovyan, Armenia

² A.B. Nalbandyan Institute of Chemical Physics NAS RA, Armenia

The interaction of N-monomethylol urea with maleic anhydride is studied. The product of this reaction forms an oligomeric monomer by condensation with chitosan. This oligomeric monomer has a capacity of copolymerization in aqueous media with other soluble monomers such as acrylic acid forming crosslinked water-swelling copolymer. The products obtained in mentioned above reactions were investigated by IR-spectroscopy and elemental analysis.

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Keywords: chitosan, maleic anhydride, N-monomethylol urea, crosslinked water-swelling copolymer.

Introduction. There are many references devoted to chitosan (CHTS) and its functional derivatives, which are of practical significance. Particularly, the works of the authors [1, 2] are about the applications of modified derivatives of chitosan used as carriers of medicinal preparations for diseased areas of a living organism. In papers [3–5] it is noted that low-molecular water-soluble fractions of chitosan are used as drugs for the treatment of various diseases (tumors, wounds, restoration of the immune system, etc.), and in the form of additives to animal feed. Recently, there has been a growing interest among researchers in the direction of the synthesis of new derivatives of chitosan, which are of practical importance. In papers [6, 7], based on a detailed study of the kinetic regularities of the grafting process, data are presented related to the modification of chitosan by grafting water-soluble monomers on it.

This article is devoted to the modification of chitosan by polymer-analog transformations grafting on it water-soluble monomers with reactive functional groups capable of copolymerizing with other water-soluble monomers. As a water-soluble monomer acrylic acid (AA) was used.

By the reaction of condensation between N-monomethylol urea (MMU) and maleic anhydride (MA) is formed the saturated monomer with terminal carboxyl group (MAMMU), which is presented below:

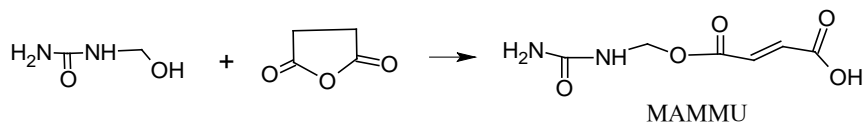
* E-mail: mejlum.yeritsyan@mail.ru

** E-mail: armarustam@gmail.com

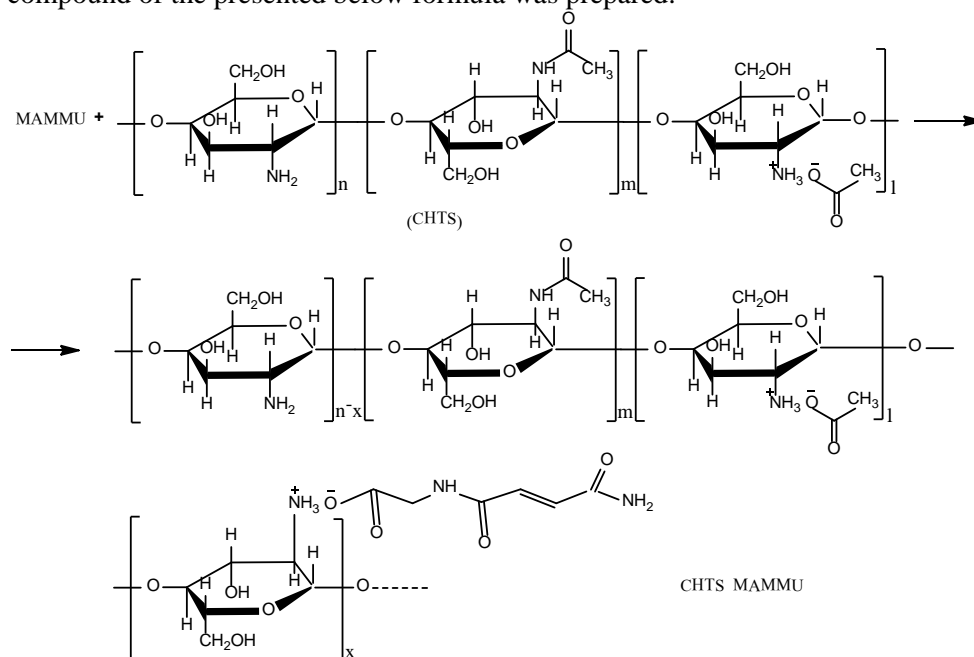
*** E-mail: valiamav@hotmail.com

**** E-mail: inessasirekanyan@yahoo.com

***** E-mail: samvelts@list.ru



By the reaction between aminoglycoside group of chitosan and MAMMU a compound of the presented below formula was prepared:



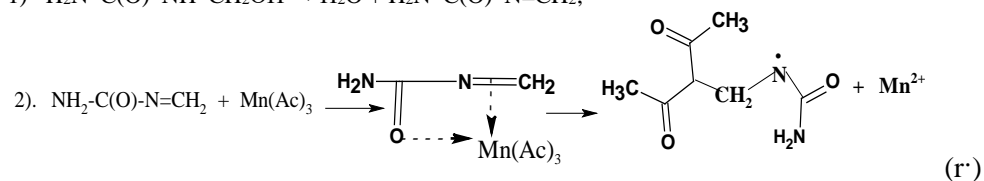
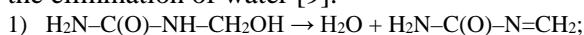
where n , m , l , x are the number of corresponding chains in chitosan.

As indicated in reference [1], $n = 0.47$, $m = 0.08$, $l = 0.45$, x is defined by the elemental analysis on nitrogen according to the formula given as follows [8]: $\text{DD} (\%) = [(N - N_0) / (N_{\text{max}} - N_0)] \cdot 100\%$, where N_0 and N_{max} are the percentage of nitrogen in the $-\text{NH}_2$ functional group of aminoglycoside chain of the CHTS molecule upon its complete transformation into an ammonium salt of NH_3^+ OR type: $[\text{R} = \{-\text{C}(\text{O})-\text{CH}=\text{CH}-\text{C}(\text{O})-\text{CH}_2-\text{NH}-\text{C}(\text{O})-\text{NH}_2\}]$, respectively. N is the nitrogen percentage in the ammonium salt of the aminoglycoside chain in the process of chitosan modification.

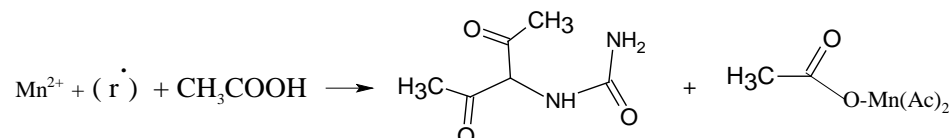
Taking into account the fact that the mole fraction of aminoglycoside chains in the CHTS molecule is 0.47, then its mass, for example, in 2 g of CHTS will be equal to 0.94 g ($2 \cdot 0.47 = 0.94$ g). Knowing the molecular mass, if aminoglycoside unit is equal to 160 g, we can calculate the number of moles of aminoglycoside units in the CHTS molecule, which is 0.0059 mol ($0.94/160$). Thus, 2 g of chitosan contains 0.0059 mol of aminoglycoside units. The calculations showed that in this case only 20% of 0.0059 mol of aminoglycoside chains in the chitosan molecule reacted with the MAMMU, and as a result, 0.00118 mol of CHTS MAMMU was obtained which is presented by the above formula. Furthermore, in the presence of the redox initiator $\text{Mn}(\text{Ac})_3$ (where Ac is the acetylacetonate radical) the graft copolymerization between acrylic acid and CHTS MAMMU was conducted.

During graft polymerization only 9.5% (0.0071 mol) of the starting acrylic acid monomer (0.075 mol) was transformed into grafted chains.

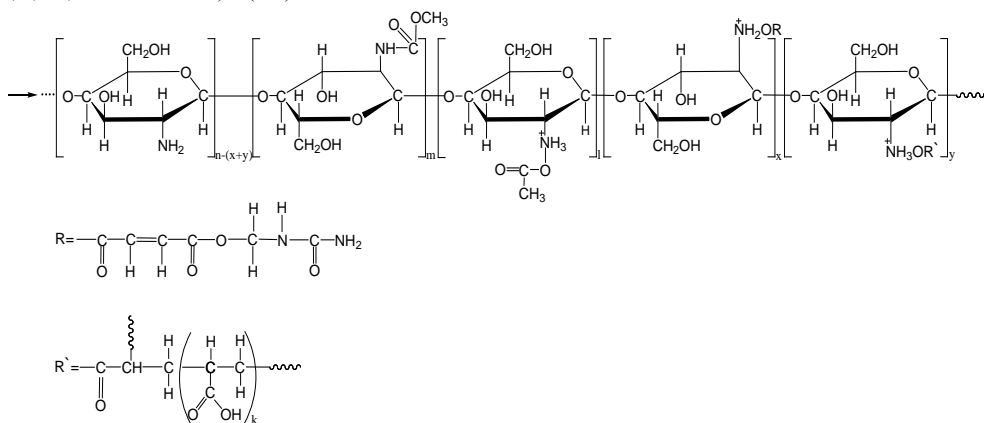
Methylene urea is prepared from N-monomethylol urea in acidic media by the elimination of water [9].



Then mono-electronic oxidation of Mn^{2+} occurs.



Graft copolymerization results in a copolymer of the following exemplary structure:



$n, m, l, x, y, k = 1, 2, \dots$

The calculations have shown that from mentioned above 0.075 mol of the initial amount of acrylic acid only 8.9% has inserted into the copolymer composition. As follows from the above data, the average number of acrylic acid units per functional group of CHTS MAMMU is 714.

The following absorption regions are found in IR spectra of the copolymer: 1340–1400, 1550, 1600 cm^{-1} relates to ammonium salts of carboxylic acids, 1640 cm^{-1} corresponds to the absorption of ($-\text{CH}=\text{CH}-$) group and the region 1100–1150 cm^{-1} corresponds to valence vibrations of ($-\text{CH}_2-\text{NH}-\text{CH}_2$). The hydrogen bond appearing in the region of 2800–3400 cm^{-1} characterizes the dimers of carboxylic acids.

It should be noted that the synthesized water-swelling copolymer with a spatial structure was tested as an adsorbent for industrial wastewater treatment in order to remove heavy metal ions such as Cu^{2+} , Cd^{2+} , Fe^{3+} , Fe^{2+} , Co^{2+} , Hg^{2+} , Pb^{2+} and so forth.

Experimental Part. IR spectra of the synthesized chitosan copolymer were recorded on the spectrophotometer NICOLET/FT-IR NEXUS.

Chitosan (“Bioprogress” CJSC, Shelkovsk, RF) with an average molecular mass of about 80 *kDa*, distilled acrylic acid (fraction with a boiling point of 141°C) and Mn(Ac)₃ (of chemically pure grade) were used in the investigations. MMU was prepared according to the technique described in detail in [8].

Preparation of MAMMU. The interaction between 9 g (0.1 mol) of MMU and 9.5 g (0.1 mol) of MA was conducted by continuous stirring at the temperature 65–70°C about 30–35 min. Further, the prepared viscous mass was washed by ethanol, then with chloroform and dried at 70–75°C at a residual pressure equal to 1.5–2.0 mm Hg to constant weight. The yield was 98%. The synthesized MAMMU has a high solubility in water and is partially soluble in acetone and ethylacetate.

Preparation of CHTS MAMMU. 2 g CHTS with an average molecular mass of 80 *kDa* was dissolved in a 2% aqueous solution of acetic acid. And while stirring, 18.8 g (0.1 mol) of MAMMU was added into the reactor. The reaction was conducted for about 40–45 min without stopping the stirring. Then the water was removed under the low pressure and the content of the reactor was washed using the water–ethanol mixture (C₂H₅OH : H₂O = 2 : 1 by volume). The content of the reactor was dried under at pressure 1.5–3.0 mm Hg at 65°C to constant weight. The yield was 68%.

Graft Polymerization of AA in the Presence of CHTS MAMMU. The reactor with a volume of 100 mL was charged with 50 mL of water, 7.2 mL (0.1 mol) of AA, 2.21 g of CHTS, which were vigorously stirred at the temperature 30–35°C until complete dissolution of the compounds. Next 0.46 g (0.002 mol) Mn(Ac)₃ was added and the temperature of the mass was increased to 65–70°C without stopping the stirring. The polymerization process is conducted at this temperature for 1.5 h. The reaction mass becomes cloudy after 30 min from the start of polymerization, which indicates the beginning of the polymerization between AA and CHTS. At the end of the specified time the precipitate was separated by filtration, washed with water and alcohol, and then dried under vacuum (1.5–2.0 mm Hg) to constant weight. The water and unreacted in the polymerization process AA were removed by a water jet pump under a pressure of 10–15 mm Hg. The residue was washed with ethanol and dried under vacuum 1.5–2.0 mm Hg to constant weight. The amount of acrylic acid transformed into grafted chains (CHTS MAMMU) is calculated by subtracting of unreacted amount of AA from its initial amount.

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REFERENCES

1. Gorovoy L.F., Kislyakov V.N. *Chitin and Chitosan. Preparation, Properties and Application* (ed. K.G. Scryabin et al.). Moskva, Nauka (2002), 217–246 (in Russian).
2. Bolgov A.A. Preparation of Chitosan’s Homologous and Polymer-Analog Transformations of Them. PhD Thesis. Moskva, V. Lomonosov Academy of Chemical Technology of Moscow (in Russian).
3. Zubareva A.A., Ovchinnikova E.V., Ilina A.V. et al. *Safety and Nanomedicine*. Materials of the Second International School “Nanomaterials and Nanotechnologies in the Living Systems” (19–24.09.2011). Moscow, 76 p. (in Russian).
4. Hakobyan E.A., Margaryan A.A., Attaryan O.S., Asatryan G.S., Bazukyan I.L., Panosyan O.A., Trchunyan A.A. Antimicrobial Activity of Chitosan Films Modified with Pyrazole Carboxylic Acids. *Biological Journal of Armenia* 1 (2015), 45–49 (in Russian).

5. Perminov P.A., Kildeeva N.R., Timofeeva L.M., Abronin I.A., Babak V.G., Nikonorov V.V. Structure Formation in Chitosan Solutions in the Presence of a Cross-linking Reagent in the Preparation of Biologically Active Polymeric Materials. *Izv. Chemistry and Chemical Technology* **50** : 3 (2007), 53–56 (in Russian).
6. Yeritsyan M.L., Petrosyan G.S., Karamyan R.A., Yeritsyan L.N., Arustamyan A.M. Kinetic Features of the Grafting of Functionally Active Monomers onto Chitosan. *Russian Journal of Physical Chemistry A* **93** : 4 (2019), 639–643.
7. Yeritsyan M.L., Petrosyan G.S., Karamyan R.A., Yeritsyan L.N., Arustamyan A.M. Kinetic Regularities of Polymeric Analogue Grafting onto Chitosan. *Doklady Akademii Nauk Armenii* **119** : 1 (2019), 79–85 (in Russian).
8. Kuchina Ju.A., Dolgopyatova N.V. et al. Instrumental Methods for Determining the Deacetylation Degree of Chitin. *Bulletin of MSTU* **15** : 1 (2012), 107–113 (in Russian).
9. Nikolaev A.F. Synthetic Polymers and Plastics Based on Them. Moskva, Khimia (1964), 380 p. (in Russian).

Մ. Լ. ԵՐԻՏՅԱՆ, Ա. Մ. ԱՌՈՒՍՏԱՄՅԱՆ, Վ. Մ. ՄԱՎԻՍԱԿԱԼՅԱՆ,
Ի. Ն. ՍԻՐԵԿԱՆՅԱՆ, Ս. Վ. ԾԱՌՈՒԿՅԱՆ

ՊԱՏՎԱՍՏԱՅԻՆ ՀԱՄԱՊՈԼԻՄԵՐՄԱՐԻ ԽԻՏՈՉԱՆԻ ՍՈՂԻՖԻԿԱՑՈՒՄԸ

Հետազոտվել է N-մոնոմերթիլոլմիզանյութի և մալեինաթթվի անհիդրիդի փոխազդեցության ռեակցիան: Արդյունքում ստացված վերջանյութը փոխազդեցության մեջ է դրվել խիտոզանի հետ, որը հանգեցնում է խիտոզանի ածանցյալի՝ օլիգոմերային միացության ստացմանը: Վերջինիս համապոլիմերացումը ջրային միջավայրում ուրիշ ջրալուծ մոնոմերների հետ՝ օրինակ ակրիլաթթվի հետ, բերում է ջրում ուռչող համապոլիմերի առաջացմանը: Վերը նշված ռեակցիաների վերջանյութերը հետազոտվել են ԻԿ-սպեկտրադիտման և տարրերի անալիզի եղանակներով:

Մ. Լ. ЕРИЦЯН, А. М. АРУСТАМЯН, В. М. МАВИСАКАЛЯН,
И. Н. СИРЕКАНЯН, С.В. ЦАРУКЯН

МОДИФИЦИРОВАНИЕ ХИТОЗАНА ПРИВИВОЧНОЙ СОПОЛИМЕРИЗАЦИЕЙ

Исследована реакция взаимодействия N-монометиллолмочевины с ангидридом малеиновой кислоты, продукт которой в реакции конденсации с хитозаном приводит к образованию олигомерного мономера, способного в водной среде сополимеризоваться с другими водорастворимыми мономерами, например, с акриловой кислотой, образуя сшитый, водонабухающий сополимер. Продукты вышеуказанных реакций исследованы методами ИК-спектроскопии и элементного анализа.