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SYNTHESIS OF POLYMERS BASED ON MILK AND LEMON OXYACIDS AT COVID-19 CONDITIONS

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Abstract: *New monomers: acryl amide – N- methylen lactic acid and acrylamide-N-methylene citric acid was synthesized and it's chemical structure was determined by physico-chemical methods. Water-soluble polymers on the base of this monomers were obtained.*

Key words: *AA-N-MCA-acrylamide-N-methylene citric acid, AA-N-MLA-akrilamid-N-methylenelactic acid, polymer.*

INTRODUCTION

In recent years, of particular interest are water-soluble and water-swelling polymers, the behavior of which in aqueous media significantly depends on the nature of the solvent, the pH of the medium, the presence of various substances, temperature, and other factors. Such polymers are promising for use in medicine, biotechnology, electronics (for creating sensors and sensors), for solving environmental problems, etc. [1-3].

One of the methods for obtaining such polymers is the radical polymerization of monomers containing various functional groups in the side chain [4].

This work presents the results of a study on the synthesis and radical polymerization of a new monomer based on lactic and citric acid - acrylamido N-methylene lactic acid (AA-N-MMK), acrylamido-N-methylene citric acid (AA-N-MLA). The choice of this research object is due to the fact that polymers and copolymers obtained by polycondensation of glycolic and lactic acids, due to their harmlessness, are widely used in biotechnology and medicine [5].

In addition, previously conducted studies on the synthesis of monomers and carbochain polymers based on another natural hydroxy acid - glycolic acid, have shown their promise. Polymers synthesized on the basis of unsaturated derivatives of glycolic acid exhibited pH-sensitive properties and had low toxicity and were not allergens [6].

Experimental part

Synthesis of acrylamido-N-methylene lactic acid. In a two-headed flask with a stirrer were placed 15 g (0.21 mol) of acrylamide, 20 ml of a 40% formaldehyde solution (0.27 mol), 50 ml of a 40% aqueous solution of lactic acid (0.22 mol) and 0.03 g of hydroquinone. The mixture was stirred at 323K for 3 hours. Water was evaporated in vacuum, the monomer was dried over calcium chloride, washed first with chloroform and then with acetone. The purity of the monomer was determined using the method of thin layer chromatography. For this, chromatography was performed on UV-254 Silufol using an ethyl alcohol: acetone separation system in a 2: 1 ratio. The monomer appeared as one spot with $R_f = 0.56$. The resulting monomer is a yellowish, viscous liquid that dissolves in water, alcohol, but does not dissolve in chloroform, acetone and non-polar solvents.

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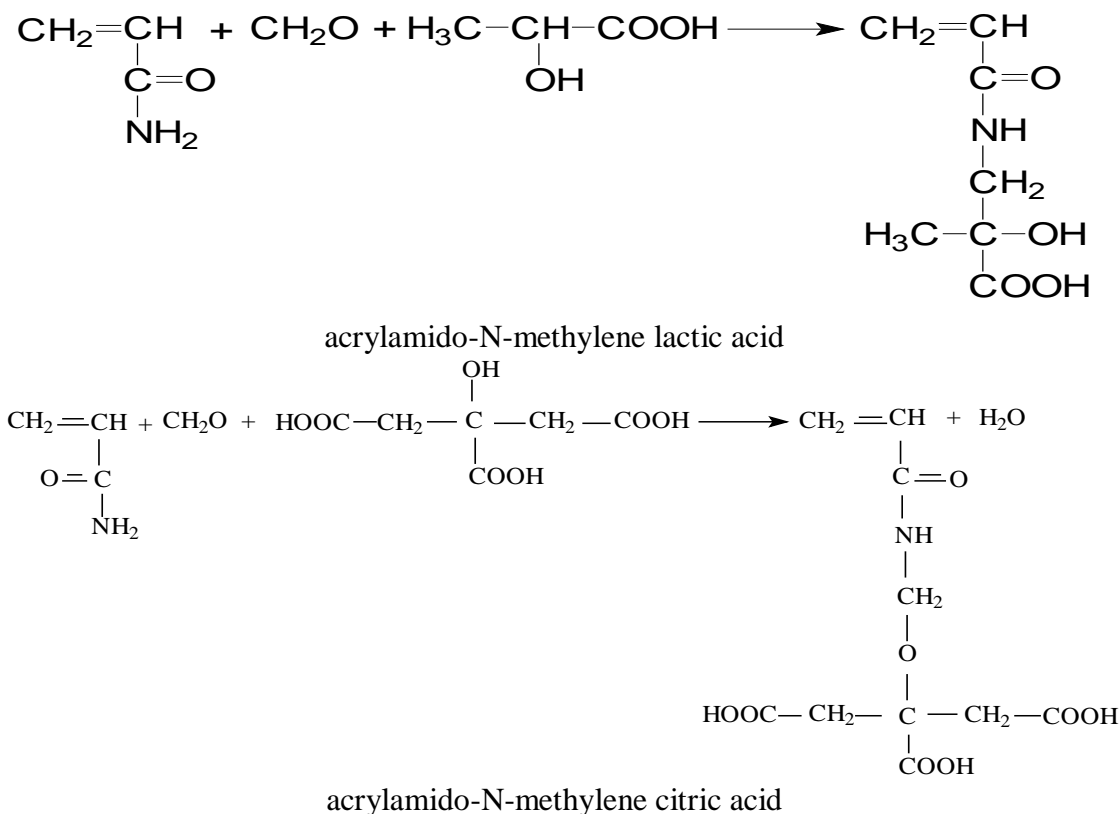
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Synthesis of acrylamido-N-methylene citric acid. Acrylamide N - methylene citric acid (AA-N-MLA). 7.1 g (0.1 mol) of acrylamide, 3 g (0.1 mol) of formalin, 19.2 g (0.1 mol) of citric acid and 0.03 g (0.002 mol) of hydroquinone were placed in a two-necked flask with a stirrer. The mixture was stirred at 333K for 3 hours. Water was evaporated from the obtained product using a water-jet pump at a temperature of 333K. The target product was purified from unreacted components by sequential extraction with carbon tetrachloride and chloroform. The product yield was 70%.

Physicochemical studies of monomers and synthesized polymers. IR spectra were recorded on a Specord IR-75 spectrometer in the range 4000 - 400 cm⁻¹ (KBr). PMR was recorded on a UNITY Plus 400 spectrometer (Varian), 0 - HMDS. The density of monomers and polymers was determined by the pycnometric method [7]. The kinetics of radical polymerization was studied by the dilatometric method. To calculate the conversion of monomer to polymer, a contraction coefficient of 0.16 was used. Potentiometric titration of the monomer and polymer was carried out in thermostated cells on an EV-74 universal ion meter, which was preliminarily calibrated against standard buffer solutions.

Results and its discussion:

In the synthesis of AA-N-MMC and AA-N-MLC, the Mannich reaction was used [8]. In this reaction, acrylamide interacts with formaldehyde to form methyolacrylamide, the latter condensing with lactic acid forms AA-N-MMK according to the following scheme:



When studying the dependence of the monomer yield on the ratio of the starting reagents, it was found that the highest yield ($\approx 62\%$) AA-N-MMC and ($\approx 70\%$) AA-N-MLK is observed practically at equimolar ratios of the starting components. The most acceptable method for the synthesis of AA-N-MMK and AA-N-MLK is the simultaneous loading of the starting components and heating the reaction mixture at 60 ° C for 3 hours with constant stirring. The chemical structure of the synthesized monomer was identified using IR and PMR spectra, calculations of molecular refraction, and determination of the acid number. Some physicochemical parameters of the obtained monomer are presented in table 1..

Table 1

Some physical and chemical parameters of acrylamide-N-methylene lactic acid

Monomer	Elemental composition%											
	MR, cm ³ / g		n _D ²⁰	d ₄ ²⁰ g / cm ³	C		H		N		Kis. number	
	found	deducti on			foun d	deducti on	found	dedu ction	найд	dedu ction	foun d	dedu ction
AA-N-MMK	41,5	42,0	1,43 12	1,05	48,5	49	6,3	6,8	8,5	8,8	230	231
AA-N-MLK	79,56	80,06	1,51	1,31	43, 6	48	4,7	4,9	5,1	5,4	17 2,6	174, 7

The IR spectra of the monomer are characterized by absorption bands in the range of 3500-3000 cm⁻¹, corresponding to both stretching vibrations - OH and amide groups, which complicates their accurate identification. The absorption band due to the carbonyl group of the carboxyl appears near 1750 cm⁻¹, the deformation vibrations of the NH group are characterized by an absorption band in the region of 1500 cm⁻¹, the absorption band near 1690 cm⁻¹ characterizes the stretching vibrations of the -C = C- bond conjugated with C = About the group.

In the PMR spectra of the monomer, groups of signals of the acrylic fragment are observed at 6.15 ppm. (2 H) and 5.875 ppm. (1 H) and two equivalent doublets with a splitting of 14 Hz belonging to the protons of the NCH₂ group with centers at 2.9 ppm. (equatorial 1H) and 2.75 ppm. (axial 1H). signal at 4.88 ppm belongs to the protons of the NH, OH group. The presence of a triplet from the protons of the CH₃ group is also observed at 1.4 ppm. two quartets with different intensities in the area of 4.3 ppm

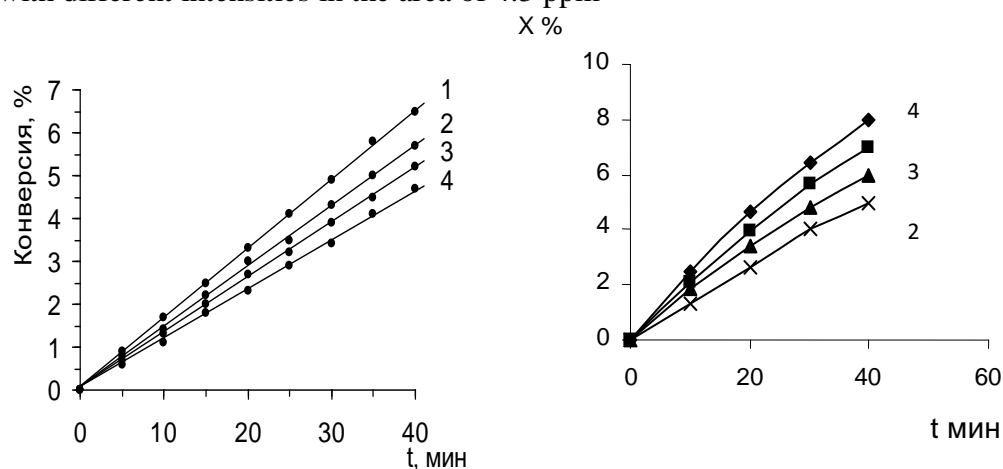


Fig. 1. Kinetics of AA-N-MMK polymerization in water at various initiator concentrations. ($[M] = 0.6 \text{ mol / l}$, $T = 333\text{K}$) 1, 2, 3, 4 - the concentration of the initiator is 0.6×10^{-2} ; 0.48×10^{-2} ; 0.36×10^{-2} ; $0.24 \times 10^{-2} \text{ mol / l}$, respectively, and AA-N-MLK 1, 2, 3, 4 - the concentration of the initiator 6×10^{-3} ; 4.8×10^{-3} ; 3.6×10^{-3} ; $2.4 \times 10^{-3} \text{ mol / L}$, respectively. $[M] = 0.38 \text{ mol / l}$, $T = 333$

The radical polymerization of monomers was studied by the method of chemical initiation, in an aqueous solution using dinitrile-azo-isobutyric acid (AIBA) as an initiator by the dilatometric method, at 333 K depending on the concentration of the initiator and monomer.

In Fig. 1.2, the kinetic direct polymerizations of AA-N-MMK AA-N-MLK obtained at various concentrations of the initiator AIBN (Fig. 1) and monomer are rearranged. It can be seen that with an increase in the concentration of both the initiator and the monomer, the rate of

polymerization increases. From the logarithmic dependences of the polymerization rate on the concentration of the initiator and monomer, the reaction orders were calculated with respect to the concentrations of the initiator and monomer, which are 0.5 and 1.4, respectively.

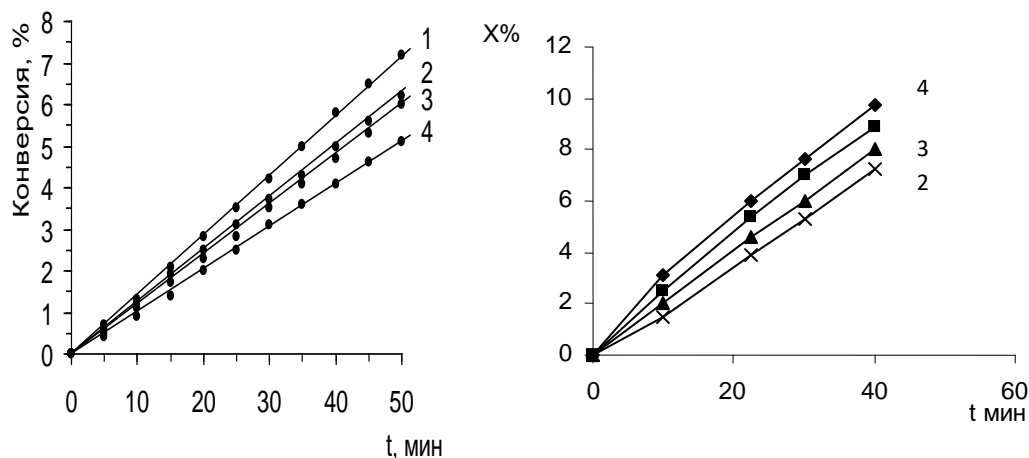


Fig. 2. Kinetics of AA-N-MMC and AA-N-MLC polymerization at various monomer concentrations. ($[I] = 0.6 \times 10^{-2}$ mol / l, $T = 333K$) 1,2,3,4-monomer concentration 1.08; 0.84; 0.6; 0.36 mol / L, and 1,2,3,4-monomer concentration 0.23, 0.38, 0.54, 0.69 mol / L, respectively. ($[I] = 6 \times 10^{-3}$ mol / l, $T = 333$)

The difference in the order of the reaction with respect to the monomer from the theoretical - the first, during polymerization of the monomers indicates the association of this monomer, which is characteristic of carboxylic acids and amides. Thus, the general equation for the rate of radical polymerization of monomers in an aqueous solution is as follows:

$$\text{AA-N-MMK } V = K \times [I]^{0.5} \times [M]^{1.37}$$

$$\text{AA-N-MJK } V_n = K_m \times [I]^{0.47} \times [M]^{1.5}$$

Thus, in this work, for the first time, a new monomer based on lactic acid, acrylamido-N-methylene-lactic acid, acrylamido-N-methylene citric acid, was synthesized and the kinetics of its radical polymerization in various media was studied. The possibility of controlling the rate of radical polymerization of this monomer by changing the nature of the reaction medium has been shown. It was found that the reactivity of the monomer under study during radical polymerization is much lower than that of acryloyl glycolic acid, a compound where the hydroxy acid is linked to the vinyl group by an ester bond. This difference in the activities of these monomers is due to the different bond rigidity and electronegativity of the atoms linking the substituent with the vinyl group of the monomer.

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