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**Research Article**

# Synthesis of polymeric derivatives of lactic acid by chemical transformations of polyacrylamide

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

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

## INTRODUCTION

In recent years, water-soluble and water-swellable polymers are of particular interest, the behavior of which in aqueous media substantially 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 detectors and sensors), for solving environmental problems, etc. [1-3].
One of the methods for producing such polymers is the radical polymerization of monomers containing various functional groups in the side chain [4]. This paper presents the results of a study on the synthesis of a new monomer based on lactic acid - acrylamide-N-lactic acid (AA-N-MK). The choice of this object of study is due to the fact that polymers and copolymers obtained by polycondensation of lactic acid, due to their safety, are widely used in biotechnology and medicine [5]. In addition, previous studies on the synthesis of monomers and carbochain polymers based on another natural hydroxy acid - glycolic, showed their perspectivity. Polymers synthesized based on unsaturated derivatives of glycolic acid showed pH-sensitive properties and had low toxicity and were not allergenic [6].

## EXPERIMENTAL PART

Acrylamide N - lactic acid (AA-N-MK). 7.1 g (0.1 mol) of acrylamide, 9 g (0.1 mol) of lactic 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 yield of the product was 77%.

AA Acrylamide N - glycolic acid (AA-N HA). 7.1 g (0.1 mol) of acrylamide, 7.6 g (0.1 mol) of glycolic 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. To remove unreacted starting materials, the product was washed first with carbon tetrachloride and then with chlorofome. The product is a pale yellow, oily substance, odorless. The product yield was 68%. Modification of PAA with lactic acid: To obtain a copolymer of 5 ml. A 4% 0.02 molar polymer solution was added with 2 ml. 80% 0.02 mol of lactic acid. The reaction was carried out for 5 hours with the addition of 5 ml. water at a temperature of 400C, with constant stirring. The resulting copolymers were isolated by precipitation in dioxane and dried under vacuum.

## DISCUSSION OF THE RESULTS

In order to obtain acrylamide derivatives of natural hydroxy acids, monomers were synthesized - acrylamido-N-glycolic and lactic acids (AA-N – HA, AA – N – MK). The synthesis of monomers was carried out according to the method described in [7]. The monomer was synthesized in an aqueous medium by the interaction of acrylamide with the corresponding natural hydroxy acids. To exclude the interaction of acrylamide with the carboxyl group of hydroxy acids, the medium was made alkaline to pH = 8 by the addition of sodium carbonate. The reacting components were mixed at an equimolar ratio of monomers. The reaction was carried out for 5-10 hours at a temperature of 40-450C. Then the

reaction mixture was acidified with hydrochloric acid and allowed to cool in the refrigerator. The resulting monomers precipitated as white crystals. They were filtered off, dried in vacuo. Column chromatography was used to obtain pure monomers. The glass column was filled with $Al_2O_3$.

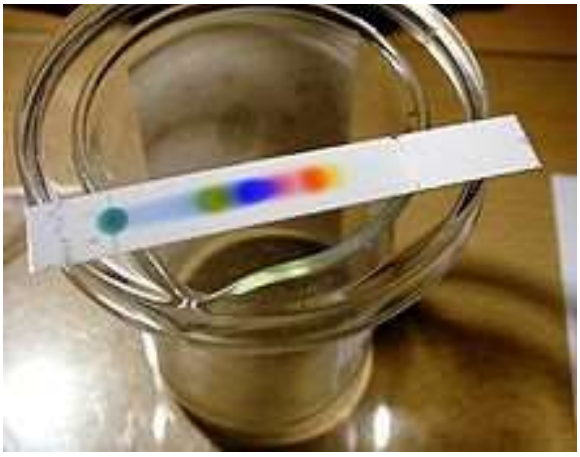


**Fig.1:**

A mixture of solvents ethylacite: alcohol in a ratio of 7:3 was used as an elucidating system. The extracted fractions were analyzed by thin layer chromatography on silifol. The value Rf=0.783 for AA-N-MMC; Rf=0.79 for AA-N-MHC. The chemical structure of the synthesized monomers was identified using IR spectra by determining the acid number by potentiometric titration. The IR spectra of AA-N-MK are shown in Fig. 1. As can be seen from Fig. 1, in the IR spectrum of AA-N-MK, absorption bands are observed in the region of 1596 cm – 1, corresponding to the double bond and 1677 cm – 1 to stretching vibrations of the –CONH group of the monomer. The intense absorption band in the 1354 cm – 1 region corresponds to the –OH of the carboxyl group, and 1717 cm – 1 to the carbonyl of the carboxyl group of the hydroxy acid. At 3753 cm – 1, an absorption band corresponding to hydroxyl groups bound by hydrogen bonds is observed, which indicates the dimerized state of the monomer.

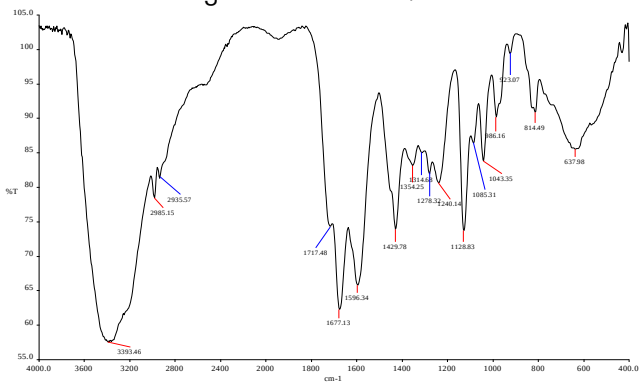



**Fig.2: IR spectrum of acrylamido-N-lactic acid**

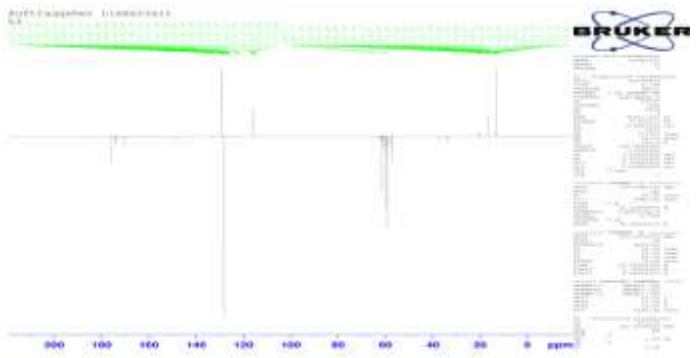



**Fig.3: NMR spectrum of acrylamido - N-glycolic acid**

The structure of the obtained monomers was also proved by NMR spectroscopy. The PMR spectra (Figs. 2 and 3) contain signals of double-bond protons of 6.2-6.5 ppm, signals of protons of $CH_2$ and CH groups with various substituents (carbon, nitrogen, oxygen) in the range of 3.5-4 5 ppm In the $^{13}C$ NMR spectra of the compounds (Figs. 4 and 5), 20 ppm signals of a carbon atom of a methyl group, 60 ppm signals of carbon atoms of the hydroxyl group. 100-110 ppm signals of carbon atoms of a double bond. Signals of carbon atoms of the carboxyl group at 180 ppm The presence of carboxyl groups in the monomers was also confirmed by potentiometric titration. Based on published data, NMR spectroscopy and potentiometric titration, the reaction of the interaction of acrylamide with hydroxy acids can be represented by the following scheme: where R = H - for the glycolic derivative, R = $CH_3$ - for the lactic acid derivative

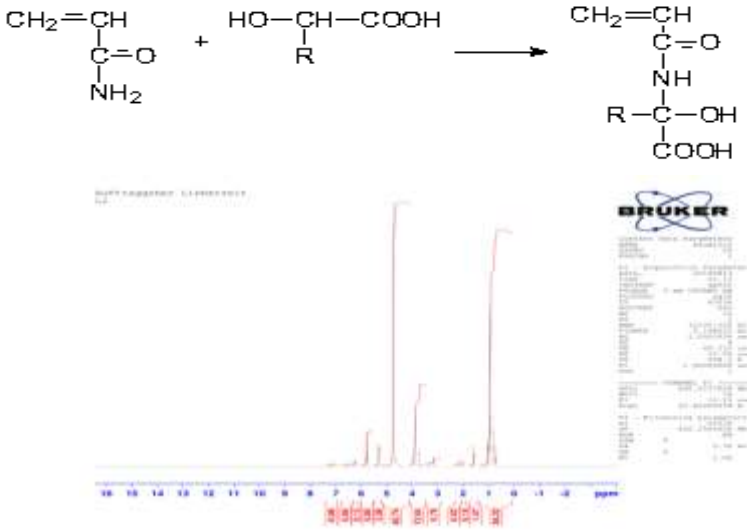



**Fig.4: PMR spectrum of acrylamido-N-glycolic acid**

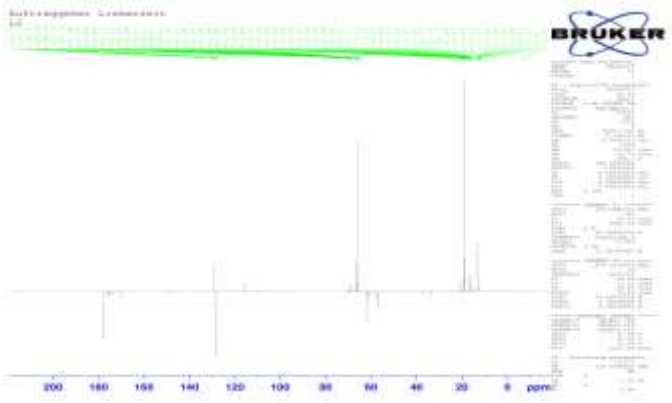



**Fig.5: NMR spectrum of acrylamido-N-lactic acid**

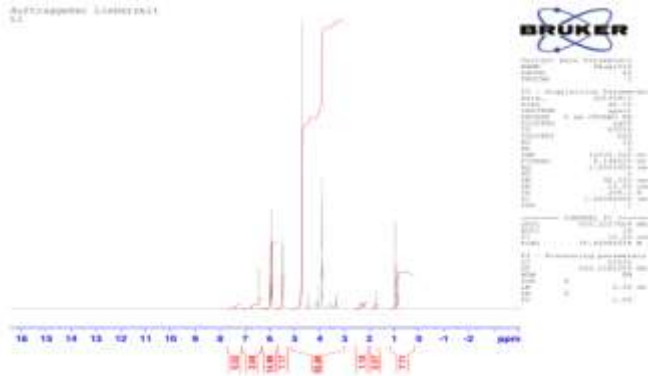



**Fig.6: 13C NMR spectrum of acrylamido-N-lactic acid**

The structure of the obtained monomers and their molecular weight was determined in the same way using chromatography-mass spectroscopy. Figure 6 shows the gas chromatography and mass spectra in which 185,200 signals corresponding to the mass of the $CH_2$=CH-CO-$NH_2^+$- C(OH)($CH_3$)-COONa fragment is observed, 163,200 corresponding to the mass of the above fragment without the Na + ion. When the $OH^-$ group is removed, a fragment with a mass of 145,200 is formed; separation of CH2 = CH group leads to the formation of a fragment with a mass of 119,200. The spectrum also shows signals at 72 - corresponding to the molecular weight of acrylamide and 91 - corresponding to the molecular weight of lactic acid, 18,300 - water molecule. Thus, chromato-mass spectroscopic studies completely prove the structure of the obtained monomer. To obtain polymers, the obtained monomers were subjected to radical polymerization in an aqueous medium. Potassium persulfate was used as an initiator. The resulting polymers were isolated by precipitation into isopropyl alcohol and dried in vacuo. Oxyacid polymers are white, soluble, powdery substances in water.

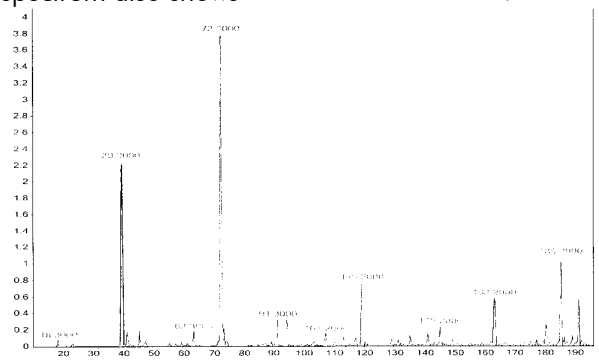
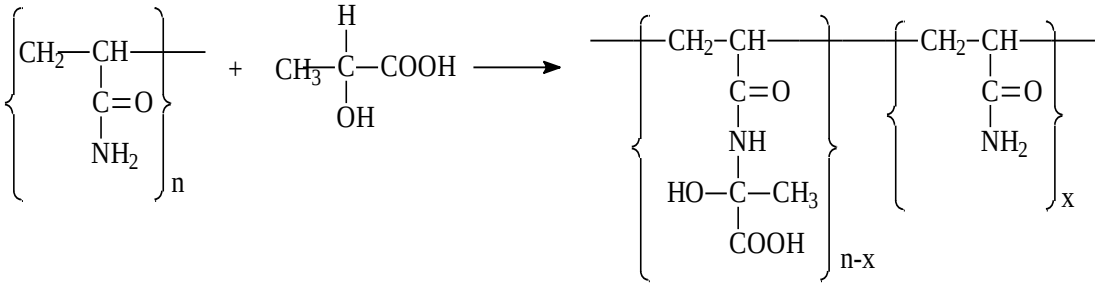


**Fig.7: Chromatomass spectrum of acrylamide-N-lactic acid**

As already noted in the literature review, PAA derivatives with carboxyl groups are widely used in various branches of science, economics, and social spheres. In this regard, in order to obtain derivatives of PAA containing carboxyl groups in the side chain, the interaction of PAA with lactic acid was studied. This reaction can be represented by the following scheme:



Polyacrylamide (PAA) was obtained by radical polymerization of acrylamide in an aqueous medium in the presence of potassium persulfate (The production reaction is given in the literature review p.9). As can be seen from the scheme, a polymer containing carboxyl groups is formed as a result of the reaction; therefore, the degree of conversion of acrylamide groups to carboxyl-containing groups was determined by the potentiometric method. The structure of the obtained polymer was identified by IR spectroscopy (Fig. 7). In the IR spectra of the modification product, 1730 cm –1 are observed, a new absorption band corresponding to the carbonyl of the carboxyl group of lactic acid is observed. In this case, a decrease in the intensity of the absorption band at 1660 cm –1 of the corresponding carbonyl amide group of the polyacrylamide is observed.

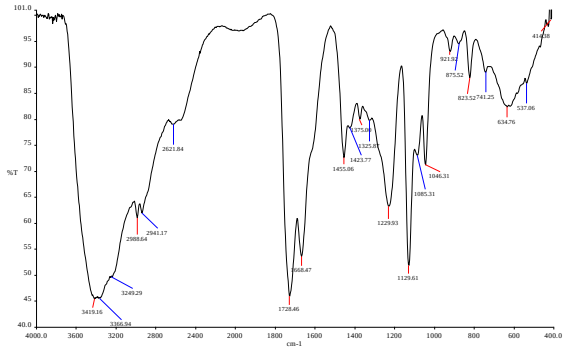


**Fig.8: IR spectrum of the product of the interaction of PAA with lactic acid.**

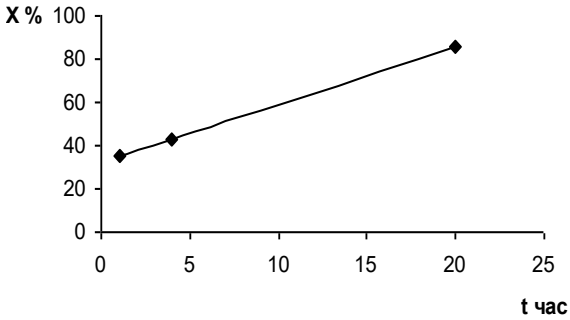



**Fig. 9 The dependence of the degree of conversion of AA groups in AA-N-MK on the duration of the reaction**

Figure 9 shows the dependence of the conversion of the amide groups of the polymer into acrylamide milk groups on the reaction time. T = 333; [PAA-N-MK] = 1.5 mol / l; [MK] = 3.086 mol / L We can see that with increasing reaction time the degree of transformation of AA groups of polymer into AA-N-MK groups increases, and the maximum value is reached in 22 hours. In order to determine the temperature dependence and the total activation energy of the process, we studied the reaction of the transformation of AA groups of the polymer into AA-N-MK groups at temperatures of 323, 333, and 343 K. Fig.10 shows that [PAA-N-MK] = 1.5 mol / l; [MK] = 3.086 mol / L

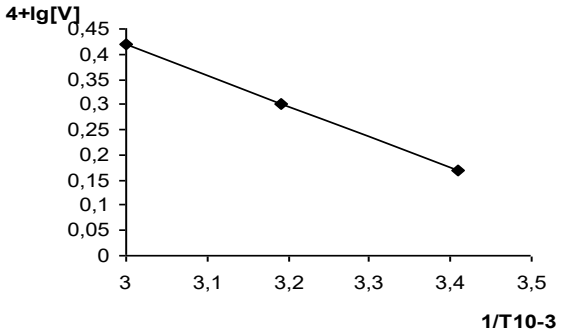



**Fig.10: Logarithmic dependence of the degree of conversion of AA groups to AA-N-MK on the inverse reaction temperature (reaction time 10 hours). The ratio of [AA]: [MK] = 1.**

As can be seen from fig. 9, the rate of the reaction under study increases slightly with increasing temperature.

**Table 1: The reaction rate and the activation energy of the modification of the polyacrylamide with lactic acid**

| T, K | V × 10-4 mol/L×s | | E, kJ / mol | |
|---|---|---|---|---|
| | PAA-N-MK | PAA-N-GK | AA-N-MK | AA-N-GK |
| 323 | 1,48 | 0,9 | 18,1 | 19,0 |
| 333 | 1,78 | 1,2 | | |
| 343 | 2,6 | 1,9 | | |

From the dependence of the logarithm of the reaction rate on the reciprocal temperature, the value of the total activation energy of the process was calculated. The found values of $E_\alpha$ for the studied system and taken for comparison PAA - glycolic acid are given in table. 1. It can be seen that the values of the activation energy of these reactions are very small, which indicates a small temperature dependence of the reaction rate.

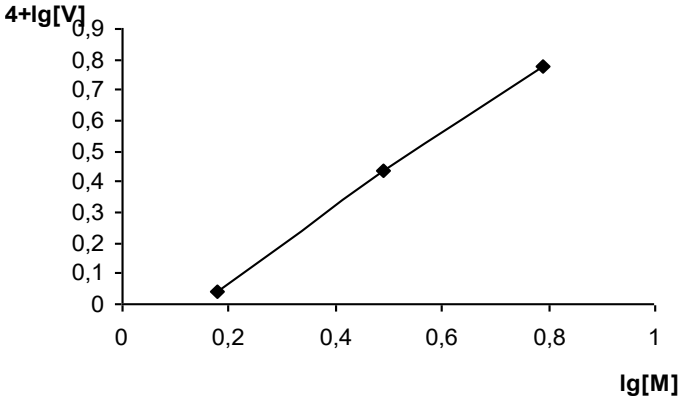



**Fig.11: Logarithmic dependence of the reaction rate of the interaction of polyacrylamide with lactic acid.**

The concentration of hydroxy acids [MK] = 3.086; 1.543; 0.79 mol / L, respectively. T = 333.

To identify the kinetic laws of the process. Fig.11 shows the logarithmic dependence of the rate of conversion of AA groups to AA-N-MK at various concentrations of hydroxy acids.

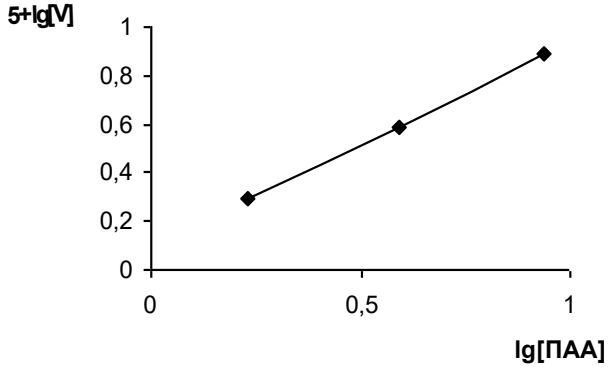



**Fig. 12: shows the logarithmic dependence of the rate of PAA-N-MK formation on the concentration of AA polymer groups.**

The concentration of the polymer [PAA] = 0.195; 0.391; 0.782 mol / L, respectively, T = 333.

From the presented data it can be seen that the reaction rate in an aqueous solution increases with increasing concentration of hydroxy acid and polymer. The reaction orders for hydroxy acid and amide groups of the polymer, determined on the basis of the data in Fig. 10 and 11 are 1.1 and 1.2, respectively. Thus, the general equation for the rate of reaction of PAA modification with lactic acid has the following form:

$$V=K[PAA]^{1,2}x[M]^{1,1}$$

It can be seen that this reaction obeys the patterns observed for homogeneous reactions, i.e. the reaction rate is proportional to the concentration of the reacting components in the first degree, and the general order is two. Thus, by the chemical conversion of polyacrylamide under the influence of lactic acid, new water-soluble polymers with carboxyl groups in the side chain are obtained.

## CONCLUSION

1. For the first time acrylamido-N-glycolic and acrylamido-N-lactic acids were synthesized on the basis of natural oxy acids. Analysis of IR-, NMR-, chromatomass spectra allows to prove the structure of the obtained monomers.
2. Modification of polyacrylamide with lactic acid produced a copolymer of acrylamido-N lactic acid. The structure of the obtained polymer is confirmed by infrared spectroscopy methods and potentiometric titration. Procedures of the given reaction on lactic acid and polymer amide groups, activation energy confirm subordination of reaction kinetics to the laws of homogeneous reactions of the second order.

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