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SYNTHESIS AND POLYMERIZATION OF N-ALLYL-N-(β -CHLOR)ALLYL ETHANIC ACID

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Abstract: The interaction of 1 mol aminoethane acid with 1 mol of allyl chloride and 1 mol of (β -chlor)allyl chloride in an aqueous solution of sodium hydroxide ($\text{pH} \geq 12$) leads to the synthesis of the new monomer – N-allyl-N(β -chlor)allylethanic acid (AEA) with a yield of $\sim 50\%$. During polymerization of AEC ($T=60-70$) in aqueous solution in the presence of ammonium persulfate (PA) initiator with a concentration of 4×10^{-4} – 5×10^{-3} mol/L, water-soluble polymers with rather high values of reduced viscosity ($[\eta_{\text{prid}}] = 0.18-0.20$ dl/g) for the above mentioned amine were obtained. It was established that the polymerization proceeded on the double bonds of diallyl groups according to the cycle-linear mechanism with pyrrolidine structure.

Keywords: aminoethane acid, allyl chloride, (β -chlor) allyl chloride, initiator, aqueous solution of sodium hydroxide, N-allyl-N(β -chlor)allylethanic acid.

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Introduction

The electro-active polymers on the basis amino acid are a new class of polymers that emerged comparatively recently. In recent years, this direction in polymer chemistry has been rapidly developing. The ion exchange sorbents, coagulants, flocculants, separating membranes, soil structurators, biopolymer models, polymeric carriers of various kinds of functional fragments – this is not a complete list of their practical applications.

There are types of polymeric materials which raise the soil fertility, regulate moisture supply to plants, decrease wind erosion of soils, stimulate plant growth and development, increase plant resistance to the effect of negative

temperatures, salinity, etc. [1-7].

At present, much attention has been paid to the synthesis of diallyl monomers, as well as polymers based on them owing to the wide range of application of water-soluble polymers; therefore, the synthesis of soluble polyelectrolyte polymers which are notable for complexes of valuable properties, in particular, amphiphilic properties.

Developing the field of synthesis and studying properties of tertiary ammonium derivatives of diallyl nature [8] in this paper the method of preparation, structure, properties and synthesis of polymers based on N-allyl-N-(β -chlor)allylethanic acid will be considered.

Experimental part

Recrystallization aminoethane acid: molecular weight 75.57, density 1.6 g/cm^3 , melting point $232-236^\circ\text{C}$. Freshly distilled allyl chloride – boiling point 45°C , n_D^{20} 1.4154,

d_4^{20} 0.9379. Freshly distilled (β -chlor)allyl chloride – boiling point 94°C , n_D^{20} 1.4600, d_4^{20} 1.2080. Ammonium persulfate (AP)

(NH₄)₂S₂O₈ products of the “chemical for analyses” brand. In all experiments bidistilled water was used. The used solvents correspond to the table specifications.

Syntheses of N-allyl-N-(β-chlor) allylethanic acid. 7.55 g (0.1 mol) of aminoethane acid is placed in a two-liter four-necked flask equipped with a stirrer, a reflux condenser, a thermometer, a dropping funnel and in cooling (not higher than 5°C) is added dropwise 7.65 g (0.1 mol) of allyl chloride and 11.1 g (0.1 mol) of (β-chlor) allyl chloride for 1 h and then 50% of aqueous solution of 12 g (0.3 mol) of sodium hydroxide. The reagent feed rate is adjusted so that the temperature in the reaction mass does not exceed 30°C. An ice water bath is used to remove excess heat. Following the addition of sodium hydroxide solution, the reaction mass is slowly heated to 70°C. The reaction mixture was neutralized (pH=7.0) with diluted hydrochloric acid. After the completion of the reaction, the reaction mixture is gradually poured into dry acetone in portions. The light yellow amino-acid as flakes is collected on the surface of the acetone. The

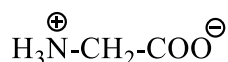
flakes are filtered on Buchner funnel, washed thoroughly with dry acetone, and then dried in an exicator over P₂O₅ to constant weight. The monomer melts with decomposition (at –287±0.2°C). The dried N-allyl-N-(β-chlor) allylethanic acid is obtained with a yield of 50-55%. Found %: C 50.72, H 6.43, N 7.22, Cl 18.59. C₈H₁₂O₂NCl, Calculated, %: C 50.67, H 6.38, N 7.39, Cl 18.69.

Polymerization of N-allyl-N-(β-chlor) allylethanic acid. An aqueous solution (0.2 mol) of the monomer in the presence of initiator (4x10⁻⁴–5x10⁻³ mol/l) was placed in a special ampoule, vacuumized and sealed. The ampoules were placed in a thermostat at a temperature 60–70°C and kept for 14-24 h. After the completion of the reaction, the reaction mixture was gradually poured into dry acetone in portions. The obtained flakes were filtered, washed thoroughly with dry acetone, and dried over P₂O₅ to constant weight. Yield – ~50%. The reduced viscosity is 0.18–0.20 dl/g. Found, %: C 50.82, H 6.47, N 7.41, Cl 18.67. C₈H₁₂O₂NCl, Calculated, %: C 50.67, H 6.38, N 7.39, Cl 18.69.

Results and discussion

It is known from the literature that it is sufficiently difficult to obtain N-alkylated α-amino acids. In the work [9], the authors showed that the basic and acidic amino acids did not react with allyl bromide nor formed the substitution products. The difficulties connected

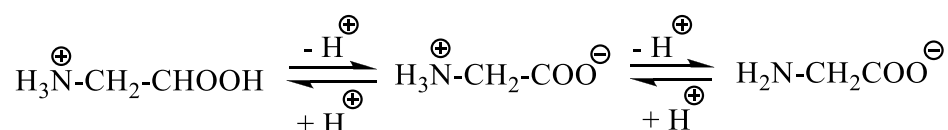
with carrying out of alkylation of α-amino acids are apparently associated with the fact that α-amino acids are amphoteric (bipolar) compounds and correspond to the general formula:



For the alkylation of α-amino acid, it must be converted to anionic form.

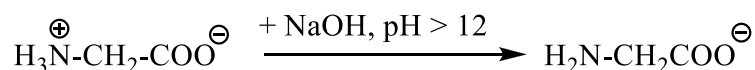
In an aqueous solution, depending on the

pH of the medium, the molecule takes the following form:



Deprotonation of the amino-acid leads to the formation of the anionic form of α-amino

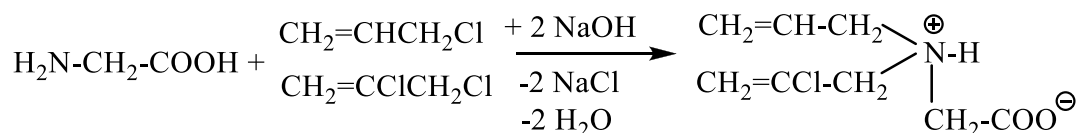
acid:



in which the basic properties of NH₂- group are enhanced, as a result of which the alkylation reaction is possible.

For synthesis of N-allyl-N-(β-chloro) allylethanic acid – diallyl monomer, the

molecule of which would contain both positively and negatively charged functional groups, we had carried out the alkylation reaction of α-amino acid with allyl chloride and (β-chloro) allyl chloride:



The identification of the product was carried out by comparison of the absorption bands of the characteristic groups of the IR spectra. The amino acid contains two functional groups – NH₂ and COO⁻, which are

characterized by absorption bands in the field of 3100–3400 cm⁻¹ for the associated group NH₂; in the field of 1725–1680 cm⁻¹ for the carboxyl group – COO⁻ (figure 1).

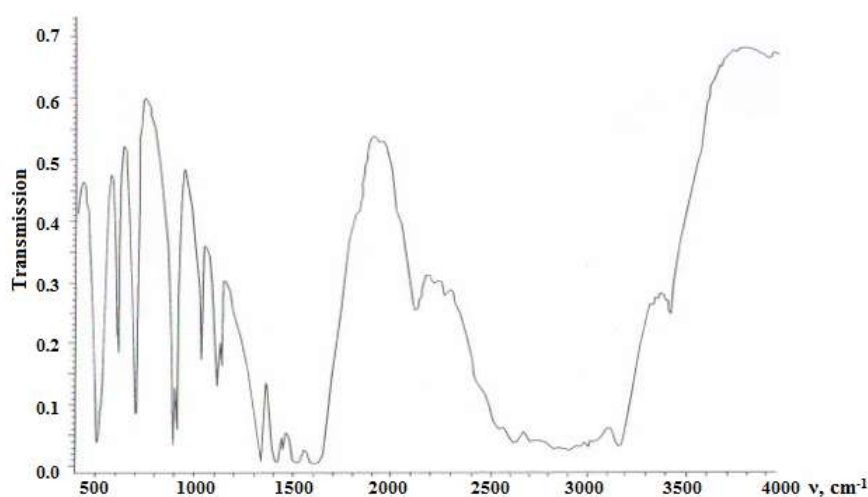


Fig. 1. IR spectrum of aminoethanic acid

In the case of the formation of N-allyl-N-(β-chloro) allylethanic acid with the analytical signal confirming the alkylation reaction is the presence of spectrum of an intensive absorption in the field of 1620 cm⁻¹ which is characteristic for the presence of C=C group (figure 2). No absorption band was observed in the field of 1750–1735 cm⁻¹ which indicates the absence of the ester COO⁻ group,

and there was an intense absorption band in the field of 1485 cm⁻¹ characteristic for deformation vibrations of R₃N⁺ – group.

Thus, it can be concluded from the analysis of IR spectra that the alkylation reaction proceeds on the amino group with preparation of the diallyl monomer in the protonated form.

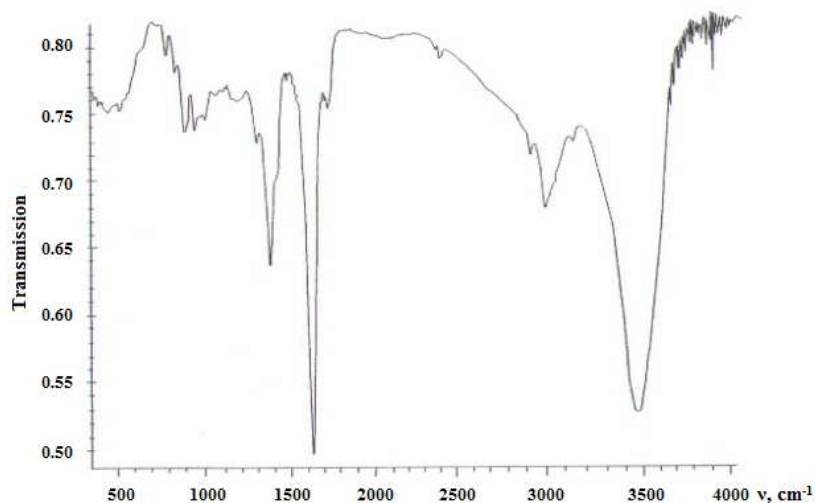
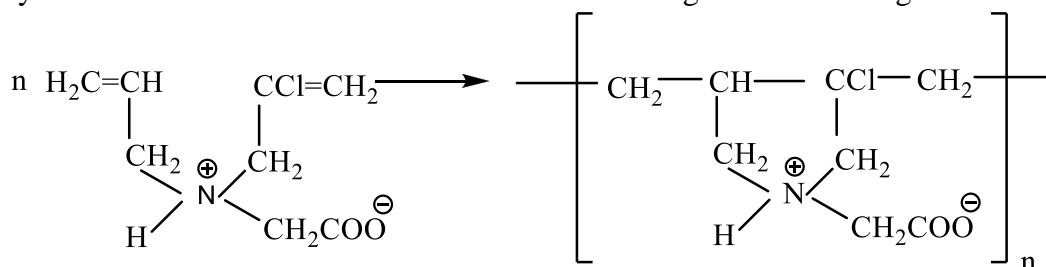


Fig. 2. IR spectrum of N-allyl-N-(β-chloro)allylethanic acid

The radical polymerization of N-allyl-N-(β-chloro) allylethanic acid was carried out in aqueous solutions under conditions radical initiation [10]. It was experimentally shown that the polymerization reaction of the above-

mentioned monomer without initiators of radical nature practically did not proceed.

The reaction of radical polymerization of N-allyl-N-(β-chloro) allylethanic acid proceeded according to the following scheme:



Results of polymerization are shown in Table.

Table. Results of the radical polymerization reaction of N-allyl-N-(β-chloro) allylethanic acid

Monomer, [M]=2 mol/l	Initiator, [I]=5×10 ⁻³ mol/l	Polymerization medium	Temperature, °C	Yield, %	Reduced viscosity (η _{red.}), dl/g
AEA	AP	Water	60	50	0.18
	AP	Water	70	62	0.20
	AP	Water-alcohol	60	40	0.08
	AP	Water-alcohol	70	44	0.10

As can be seen from Table, the highest values of the reduced viscosity were obtained in an aqueous solution as an AP initiator at a

temperature 70°C. The reduced viscosity values of the synthesized samples of polymer are 0.18÷0.20 dl/g.

Conclusions

1. The interaction of 1 mol aminoethane acid with 1 mol of allyl chloride and 1 mol of (β -chloro) allyl chloride in an aqueous solution of sodium hydroxide ($\text{pH} \geq 12$) leads to the formation of a new monomer of N-allyl-N-(β -chloro) allylethanic acid (AEA) with a yield $\sim 50\%$.
2. During the carrying out of AEA polymerization ($T=60-70^\circ\text{C}$) in an aqueous solution in the presence of AP with an initiator $4 \times 10^{-4} - 5 \times 10^{-3}$ mol/l, the water-soluble polymers with sufficiently high values of reduced viscosity ($[\eta] = 0.18 \div 0.20$ dl/g) for the indicated amine were obtained.
3. It was established that the polymerization proceeded on the double bonds of diallyl groups according to the cyclo-linear mechanism with the formation of a polymer with pyrrolidine structure.

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N-ALLİL-N-(β-XLOR)ALLİLETAN TURŞUSUNUN SİNTEZİ VƏ POLİMERLƏŞMƏSİ

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1 mol aminoetan turşusunun 1 mol allilxlorid, 1 mol (β-xlor)allilxlorid və artıqlaması ilə götürülmüş natrium hidrogenfosfatın suda məhlulunda (pH ≥ 12) qarşılıqlı təsirindən ~50% çıxımla yeni monomer – N-allil-N-(β-xlor)allilaminosirkə turşusu (AET) sintez edilmişdir. Sintez edilmiş AET –nin su mühitində ammonim persulfat (AP) iştirakı ilə, inisiatorun 4×10^{-4} – 5×10^{-3} mol/l qatılığında, polimerləşmə reaksiyası (T=60–70 °C) zamanı suda həll olan kifayət qədər yüksək özlülüklü ($[\eta_{\text{gətir.}}] = 0.18$ – 0.20 dl/q) polimer alınmışdır. Müəyyən edilmişdir ki, polimerləşmə diallil qruplarının ikiqat rabitələri hesabına tsikloxətti mexanizm üzrə pirrolidin strukturlu polimerlərin əmələgəlməsi ilə baş verir.

Açar sözlər: aminoetan turşusu, allilxlorid, (β-xlor)allilxlorid, inisiator, N-allil-N-(β-xlor)allilaminoetan turşusu.

СИНТЕЗ И ПОЛИМЕРИЗАЦИЯ N-АЛЛИЛ-N-(β-ХЛОР)АЛЛИЛЭТАНОВОЙ КИСЛОТЫ

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Взаимодействием 1 моля аминоэтановой кислоты с 1 молем хлористого аллила и 1 молем хлористого (β-хлор)аллила в водном растворе едкого натрия (pH ≥ 12) синтезирован новый мономер – N-аллил-N-(β-хлор)аллилэтановая кислота (АЭК) с выходом ~50%. При проведении полимеризации АЭК (T= 60–70°C) в водном растворе в присутствии инициатора – персульфата аммония (ПА) с концентрацией 4×10^{-4} – 5×10^{-3} моль/л получены растворимые в воде полимеры с достаточно высокими значениями приведенной вязкости ($[\eta_{\text{привед.}}] = 0.18$ – 0.20 дл/г) для указанного амина. Установлено, что полимеризация протекает по двойным связям диаллильных групп по циклолинейному механизму с образованием полимера с пирролидиновой структурой.

Ключевые слова: аминоэтановая кислота, хлористый аллил, хлористый (β-хлор)аллил, инициатор, N-аллил-N-(β-хлор)аллилэтановая кислота.