SYNTHESIS AND POLYMERIZATION PROCESSES OF 1-CHLORINE-3- PIPERIDINE -2-PROPYLMETHACRYLATE MONOMER

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SYNTHESIS AND POLYMERIZATION PROCESSES OF 1-CHLORINE-3-PIPERIDINE -2-PROPYLMETHACRYLATE MONOMER

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Abstract: *An amino alcohol was synthesized on the basis of piperidine and epichlorohydrin. The esterification reaction of methacrylic acids with the obtained amino alcohol was studied. In order to identify optimal synthesis conditions, the influence of temperature, reaction duration and ratio of reactive reagents was investigated. The processes of obtaining unsaturated esters by esterification reactions with 1-chlorine-3-piperidine-2-propanol and acrylic-, methacrylic acids have been studied. The effect of monomer concentration on the rate of polymerization reaction and the yield of polymer formation was studied . The radical polymerization of a new monomer with a piperidine cycle in the presence of a nitrogen-containing initiator in the environment of organic solvents was investigated. The influence on the polymerization process of such factors as the nature of the solvent, temperature, monomer and initiator concentration is studied. The main kinetic and energy parameters of the homopolymerization reaction are determined. The found values of the reaction orders for the monomer and initiators are 1.5 and 0.56, respectively, and the process activation energy is 59.8 kJ / mol. A synthesized crosslinked high molecular compound based on 1-chloro-3-piperidino-2-propylmetacrylate. The physicochemical properties of the obtained compound were studied, the rate of swelling in water and other media, resistance to degradation, and mechanical strength were determined . 1-chlorine-3-piperidine-2-propyl methacrylate (XPPMA) ing structure IQ , PMR-spectroscopy, chromatic-mass spectrometry methods were approved. The average characteristic viscosity of poly -1-chlorine-3-piperidine-2-propyl- methacrylate was determined by viscometric method .*

INTRODUCTION.

More recently, polymers have been attracting the attention of researchers. Among the water-soluble polymers, the so-called "smart" systems have the opposite effect on changes in environmental properties - they are characterized by a first-order phase transition, which occurs with a sharp change in the relative size of the macromolecule.

Sensitive polymers have the property of target delivery of drugs to the human body and are used in the production and purification of biomolecules, as biocatalysts, in the production of microlines, sensors and membranes [1].

Among the monomers containing the amino group of acrylic and methacrylic series, the most promising is N,N-dimethylaminoethylmethacrylate (DMAEM) , based polymers have temperature and pH- sensitivity properties.

Flour copolymers are used in the production of flocculants , in the targeted administration of drugs and in the control of the rate of their release from the carrier in the human body [2], in biotechnology and other fields of medicine.

For each individual case, a clear temperature range is required when applying the thermal sensitivity property of the polymer, in which a phase transition is observed.

This section considers the effect of various parameters that characterize the polymer on the phase transition temperature, its properties in aqueous solutions of the polymer, with a special focus on the most effective different variants of the phase transition temperature h .

The traditional method widely used in the synthesis of acrylic and methacrylic polymers is free radical polymerization - it allows to obtain thermal and pH-sensitive polymers based on monomers containing amino groups of acrylic series. These polymerization reactions were carried out in aqueous and in various organic solvent environments with the use of initiators, photoinitiators and redox initiation systems, binding agents and molecular mass regulators [3; 4].

In addition to the thermal sensitive DMAEM homopolymers free radicals in the polymers DMAEM vinylcaprolactam , 2-(2- methoxyethoxy)- ethyl methacrylate [5] N-isopropylacrylamide, acrylamide, ethyl acrylamide, butyl methacrylate, and t-BMA, MMA alkilakrilatlar (C6,8,12) thermally sensitive copolymers based on acrylic acid, vinylpyrrolidone, styrene and other monomers were obtained [6-8].

In another study, DMAEA homopolymers (acrylic analogue of DMAEM) were obtained by polymerization by chain transfer on the mechanism of binding-fragmentation (reversible addition – fragmenta tion chain transfer - RAFT) [9]. DAC was used as the initiator of this reaction, methyl-2- (butyliocarbonotioil-thio) -propanoate as the chain conductor and dioxane as the solvent.

Static copolymers based on DMAEA and MA were obtained by RAFT-polymerization in the presence of chain-transmitter dodecyl-1-phenylethyl tritiocarbonate, solvent dioxane medium and initiator DAK. The polydispersity of the samples ranged from 1.15 to 1.28.

Copolymers based on DMAEM and MMA were also obtained by RAFT-polymerization method in dioxane solution and in the presence of initiator DAK. 2-cyano-2-propylbenzoditioate was used as the RAFT agent. Polymer samples exhibited monodispers molecular-mass distribution (PDI = 1.18–1.24).

In the study, new linear and star-like DEAEM polymer samples, which are hydrophobic homologues of DMAEM by atomic transfer radical polymerization (ATRP), were synthesized using the radical polymerization method [10].

The reaction was carried out in the presence of methoxybenzene in the presence of beta-cyclodextrin, hexamethyl-triethylenetetramine initiator, as well as copper (1) chloride obtained as a ligand and catalyst. The polydispersity of the samples ranged from 1.08 to 1.36.

Ethyl-2-bromoisobutyrate or α -methyl, $\bar{o}$ - (2-bromoisobutyrate) polyethylene glycol, copper bromide, hexamethyltriethylene-tetramine as a macroinitiator with catalyst, ATP method PDMAEM, and blockade of DMAEM with polyethylene polymer [11]. The synthesis was carried out in a mass of monomers, in a toluene or tetrahydrof uranium medium.

MATERIAL AND METHODS. An amino alcohol was synthesized on the basis of piperidine and epichlorohydrin. The esterification reaction of methacrylic acids with the obtained amino alcohol was studied. In order to identify optimal synthesis conditions, the influence of temperature, reaction duration and ratio of reactive reagents was investigated. Epichlorohydrin, methacrylic acid, distilled water, benzene, ethyl alcohol, chloroform, acetone were used to study the reactions based on piperidine. Below are some physicochemical parameters of the starting materials used.

Ethanol (ethyl alcohol, methylcarbinol) — CH_3CH_2OH colorless slightly mobile, odorless liquid, boiling point 78,39 °C, density 0,7893g/cm³. It was dehydrated using calcium oxide and the fraction at 78 °C was collected by driving .

Piperidine (hexahydropyridine, pentamethyleneimine) - $C_5H_{11}N$ pungent odorless liquid, density 0,862 г/см^3, T.liquid.= -7 -9℃, T. boiling.=106,17℃. Epichlorohydrin (1-chlorine-2,3-epoxypropane, 2-chloromethyloxyrane) -C_3H_5ClO is a colorless liquid with a pungent odor; T.liquid. =- 57,0 °C; T. boiling.= 117,9℃, d_4^{20}=1,18; n^{20}_D=1,4381. Methacrylic acid (propenic acid, ethylene carboxylic acid) - $CH_2=CCH_3COOH$; colorless liquid with a pungent odor; T.liquid.=12-13,5°C, T. boiling=140,9-141,6°C, 65°C/30 mm rt. st; $d^{20}_4$1,0511, n^{20}_D1,4224 The initiator DAC is recrystallized in ethanol. The viscosity of the polymer was

determined on a Ubbelode viscometer at a temperature of 20 ºC The IR spectra of the primary reagents and synthesized substances were obtained on a SHIMADZU IR-100 spectrometer.

The kinetic laws of the polymerization reaction of the synthesized monomer were studied using the gravimetric method. To do this, the required amount of monomer, solvent, initiator is added to the grounded test tubes. Prepared in a solution of 5 minutes, sent to the inert gas and the desired h temperature thermostats. After thermostatization, the reaction solution is taken into a beaker every 15 minutes using a syringe, precipitated, and the amount of polymer is determined. In this case, the degree of formation of the polymer was obtained up to 15%.
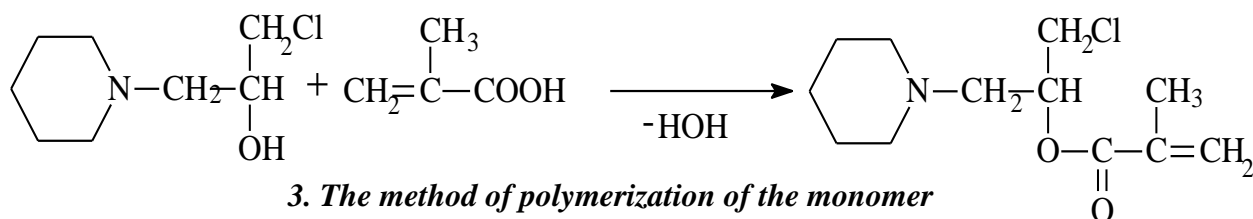
1. *Synthesis of 1-chlorine-3-piperidine-2-propanol*

The process of amino alcohol synthesis based on piperidine and epichlorohydrin occurs exothermically . In this case, the interaction of piperidine with epichlorohydrin (EXG) was carried out at a relatively low temperature in an aqueous medium. The reason why the crosslinking reaction of piperidine and epichlorohydrin was studied at temperatures of -1 to -5 ^{0}C was that the temperature was kept negative at higher temperatures to prevent the formation of quaternary ammonium oligomers and amino alcohol synthesis, and 1-chlorine-3-piperidine-2-propanol (XPP) was synthesized [12] .
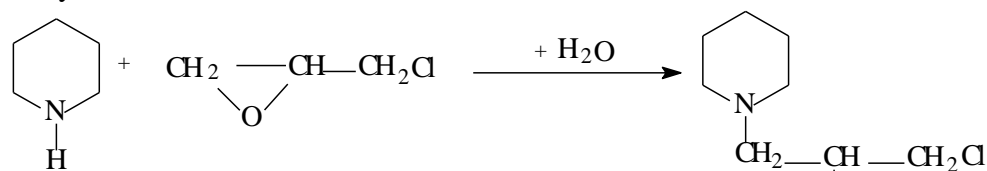

2. *Synthesis of monomer 1-chlorine-3-piperidine-2-propylmethacrylate*

Following the 1-chlorine-3-piperidino-2-propanol molecule gidroksil the existence of the group and it is because of the relatively weak nucleophiles characteristic ON-group combination reactions expected to participate in this section of the above synthesized 1-chlorine-3-piperidin-The process of synthesis of unsaturated esters based on the et t erification reaction of methacrylic acid with 2-propanol was studied [13] . The reaction was carried out at a temperature of 80 º C for 3 h. The synthesis processes of 1-chlorine-3-piperidine-2-propyl methacrylate were studied. The esterification reaction of methacrylic acid with 1-chlorine-3-piperidine-2-propanol can be expressed by the following scheme:

3. *The method of polymerization of the monomer*

Radical polymerization of the synthesized 1-chlorine-3-piperidine-2-propyl methacrylate has been studied [14] . The process was studied in different solvent media in a temperature range of 50–80 º C. In this case, the degree of formation of the polymer is obtained in the range of 5-15%.
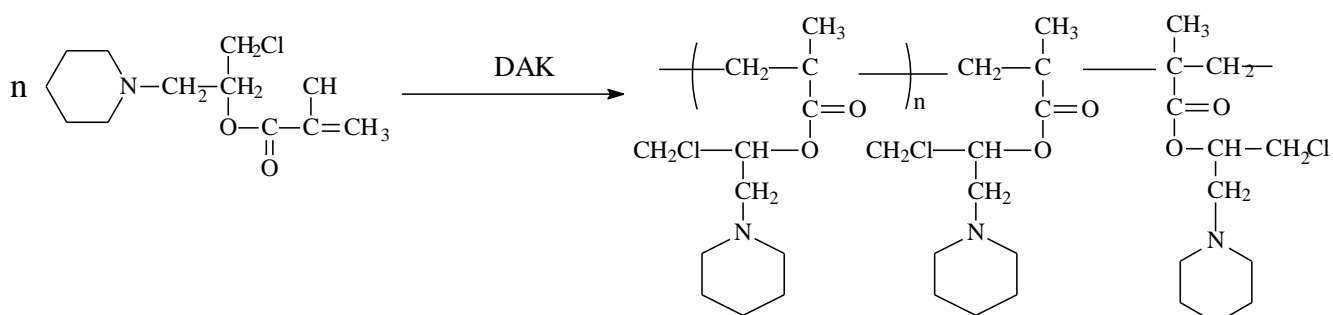
Thermoanalytical study of the synthesized samples was performed on a Netzsch Simultaneous Analyzer STA 409 PG (Germany) equipped with K-type thermocouple and (Low RG Silver) aluminum crucibles. IR spectra were obtained on an IR-Fure SHIMADZU spectrometer.

Mass spectrometry. Mass spectra of 6420 TripleQuadLC / MS (AgilentTechnologies, USA) were obtained using the APCI-ionization method (chemical ionization at atmospheric pressure).

Determination of viscosity of polymer solutions. The study was performed on a clean dried Ubellode viscometer. The study of the kinetics of the polymerization reaction was performed by the gravimetric method.

RESULTS.

1-chlorine-3-piperidine-2-propyl methacrylate (XPPMA) ing structure   IR , PMR-spectroscopy, chromatic-mass spectrometry using methods approved .

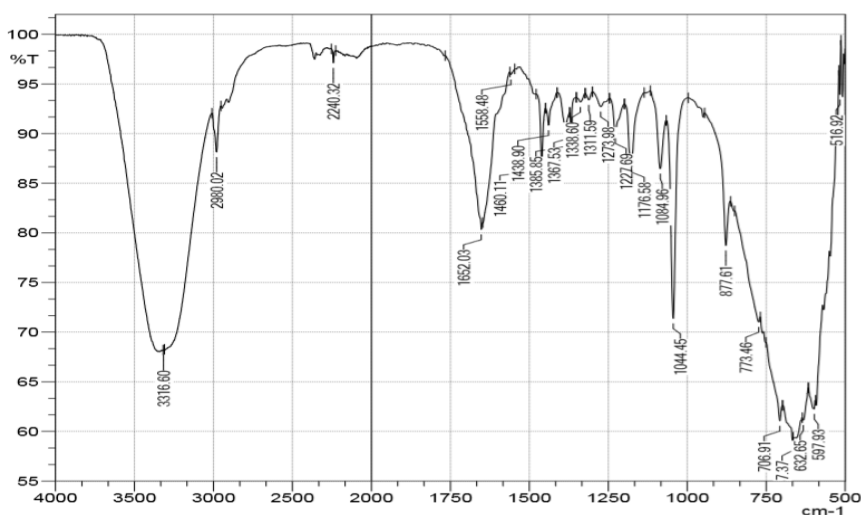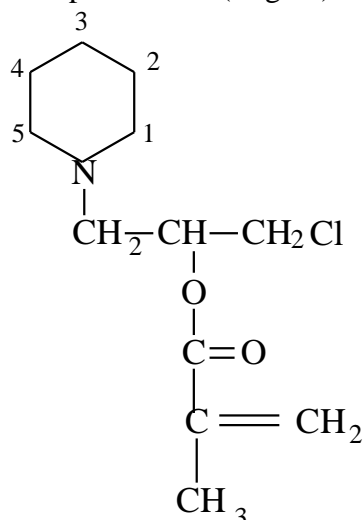**Fig. 1. IR spectrum of 1-chlorine-3-piperidine-2-propyl methacrylate .**

The IR spectrum of XPPM showed the following absorption lines, cm^{-1}: v(C-N) 3316; v (CH$_2$) and (CH$_3$) 2980; v (C=O) 1652; v (C=C) 1558; v (C-O-C) asymm 1227-1273 and simm 1044.

The structure of 1-chlorine-3-piperidine-2-propyl methacrylate (XPPM) was also studied using the PMR spectroscopic method (Fig. 2).
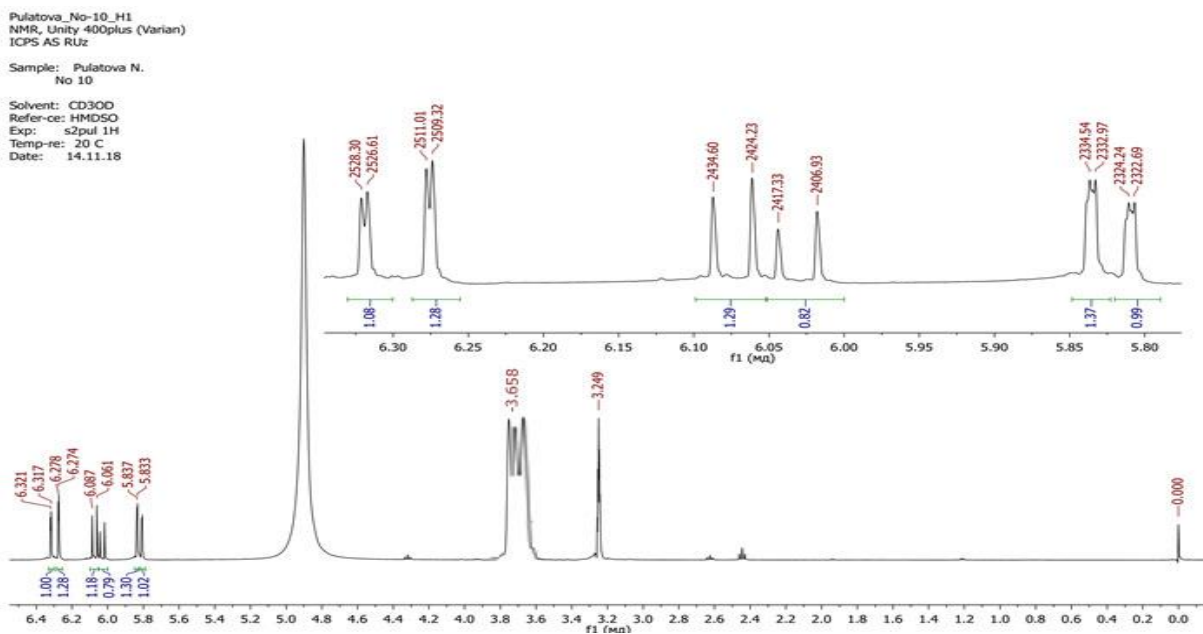
Fig. 2. PMR spectrum of 1-chlorine-3-piperidine-2-propyl methacrylate .

In the PMR spectrum of 1-chlorine-3-piperidine-2-propylmethacrylate in Figure 3.1.9, we take as the basis of the piperidine ring, the carbon atoms on both sides of the nitrogen atom in the piperidine ring have the same strength so that carbon atoms 1 and 5 are carbon atoms 2 and 4. represents areas of absorption in the same area. Hence, the double-double signals of protons located on 1.5-carbon atoms are 6.321–6.317 m.u. in the field, the doublet signals of the protons on the 3-carbon atom 6.1 In the field, the doublet-doublet signals of the protons located on the 2,4-carbon atoms 6.278-6.274 m.u. observed in the fields. The singlet signals of the protons of the C atom in HC-Cl are 6.03 m.u. fields, and the doublet of the protons of the C atoms in the C = C bond is 6.05 m.u. the doublet signals of the protons in H_2C-Cl in the fields are 4,314 m.u., and the triplet signals of the protons in CH_3 are 3,658 m.u. observed in the fields.

In the next process , the xr omato-mass spectrum, which is another method of physicochemical study of 1-chlorine-3-piperidine-2-propylmethacrylate, was expressed (Fig. 3.) .
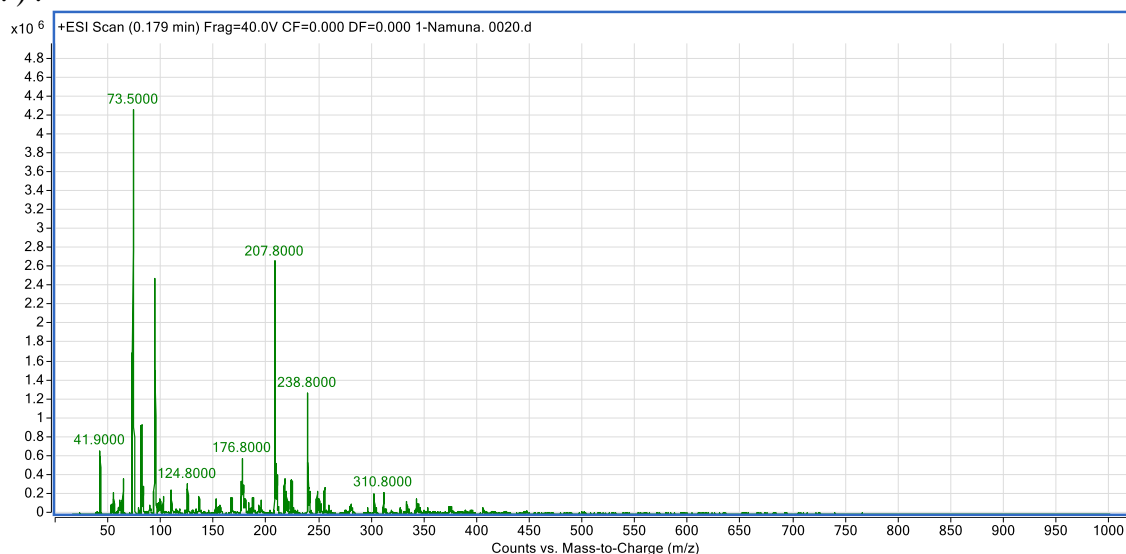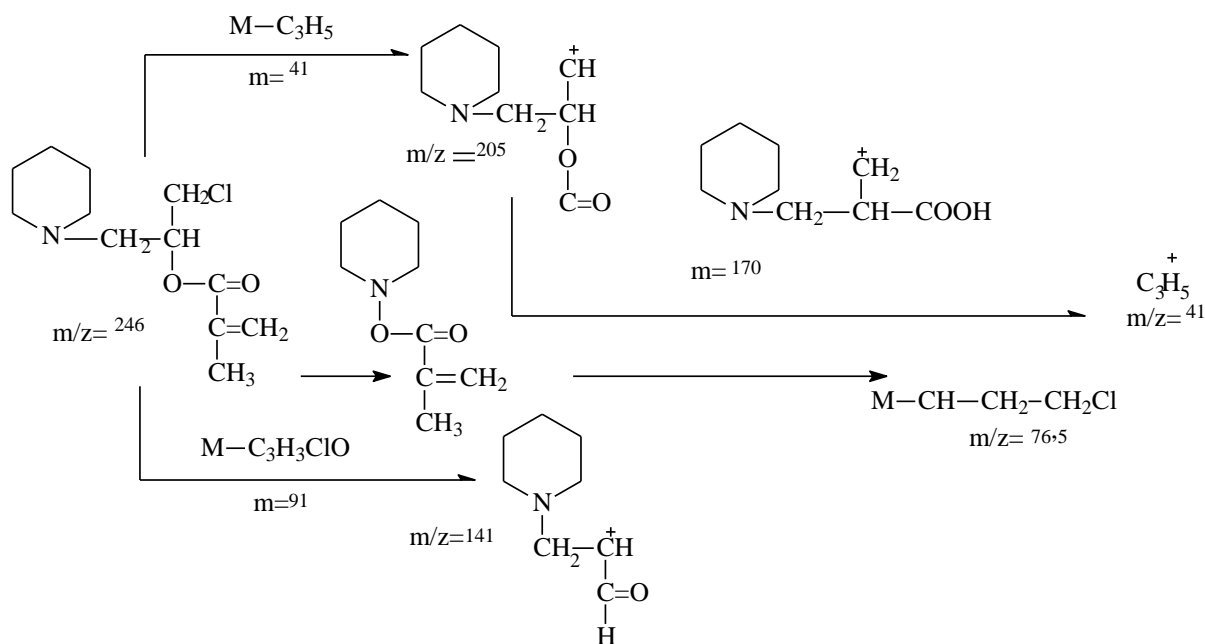

Fig. 3. Chromato-mass spectrum of 1-chlorine-3-piperidine-2-propylmethacrylate

According to these results, the products of decomposition of a macromolecule into several ions can be seen in the following scheme when a molecule of synthesized 1-chlorine-3-piperidine-2-propylmethacrylate is sent a stream of ions in the chromato-mass spectrum:

$M-C_3H_5$

m= 41

m/z = 205

m/z = 246

$M-C_3H_3ClO$

m=91

m/z=141

m= 170

m/z= 41

$M-CH-CH_2-CH_2Cl$

m/z= 76,5

In Fig. 3 the chromato-mass-spectrum of 1-chlorine-3-piperidine-2-propylmethacrylate can be seen in the absorption regions corresponding to the molecular mass of the above ions.

Table 1.

Physicochemical properties of synthesized compounds

Of the substance Naming	Gross formula	Product yield, %	T boiling, °C/ mm rt. st	d^{20}_4, г/см^3	n^{20}_D	R_f
ХПП	$C_8H_{16}NOCl$	85	105	1,35	1,372	0,56
ХППМА	$C_{12}H_{20}NO_2Cl$	85	132	1,198	1,262	0,65

The kinetic laws of the radical polymerization process of 1-chlorine-3-piperidine-2-propylmethacrylate (XPPM A) were studied [14]. To determine the basic laws of the polymerization reaction, the effect of various factors: the nature of the solvent and the initiator, the concentration of the monomer and the initiator, the temperature was studied . As the initiator was used with different initiators: a zobisizobutyronitrile (DAC) and benzoyl peroxide, potassium persulfate. The rate of the polymerization reaction, the kinetics of the polymerization reaction of monomers were studied in the presence of various initiators , in an environment of organic solvents at a temperature of 50-80 °C. The nature of the solvent also affects the polymerization process. The study of the effect of solvent nature on the kinetics of the polymerization process was conducted in ethanol and dimethylformamide (DMFA) medium (Table 2). According to the results obtained from Table 2, the highest yield of polymer formation was observed when polymerization of monomers was carried out in a dimethylformamide medium in the presence of DAC . Such a phenomenon can be explained by the fact that it occurs due to an increase in the chain growth rate constant in polar solvents.

Table 2.

The effect of solvents and initiators on the polymerization process of XPPMA, temperature, time. [I] = 5·10⁻³ mol / l; [M] = 0.1 mol / l

Name of the substance	The name of the initiator	Solvent	Temperature °C	Polymerization time, minutes	Product yield,%
1-chlorine-3-piperidine-2-propyl-methacrylate	DAK	Ethanol	65	70	12.3
		DMFA	60	50	13.6
	Benzoyl peroxide	Ethanol	80	200	9
		DMFA	75	180	9.8
	Potassium persulfate	Ethanol	60	120	10
		DMFA	55	90	10.6

The radical polymerization process of 1-chlorine-3-piperidine-2-propylmethacrylate (XPPMA) was studied. The effect of the concentration of monomers on the rate of the polymerization reaction and the yield of the polymer was studied by the gravametric method. In this case, the monomer concentration was obtained in different ratios, but the process was studied without changing the initiator concentration. The results obtained in the next step are presented in the form of several graphs. The effect of XPPM A concentration on the reaction rate on the polymerization reaction rate and polymer formation yield was studied (Fig. 4).
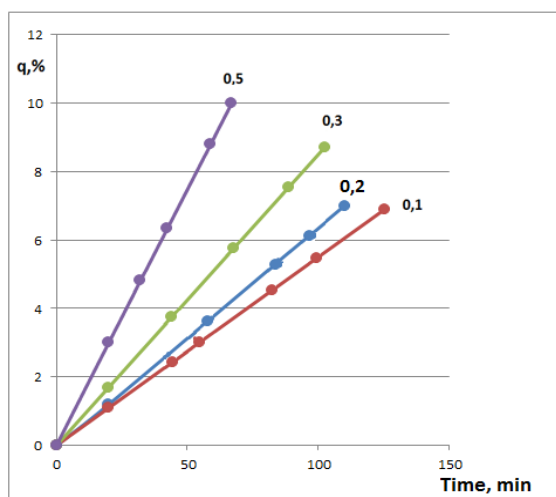

Figure 4. Polymerization of 1-chlorine-3-piperidine-2-propylmethacrylate at different concentrations (mol / l). [DAK] = 5·10⁻³ mol, T= 60 °C, solvent DMFA.
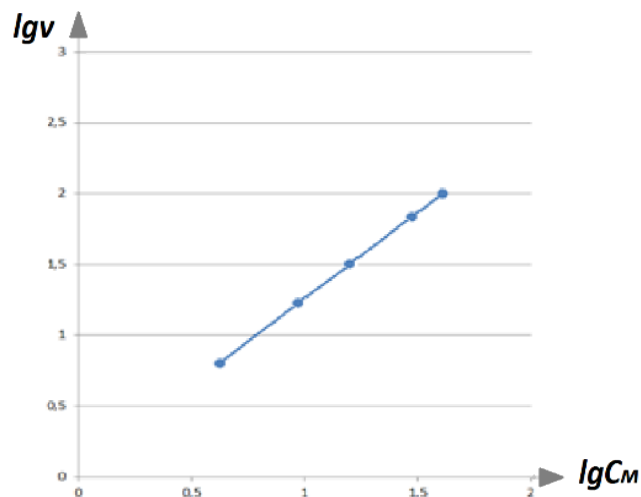
Figure 5. lg V _pol_ = f (lg [M]) dependence graph. [DAK] = 5·10⁻³ mol / l, [M], mol / l: 0.1; 0.2; 0.3; 0.5. T=60 °C, solvent DMFA.

As can be seen from Figure 4 , the reaction rate also increases with increasing monomer concentration. Based on the results obtained, it was determined that the order of the polymerization reaction on the monomer is 1.5 (Fig. 5). In subsequent processes, the effect of initiator concentration on the polymerization of the synthesized monomer was studied.

The results obtained on the effect of initiator concentration on the polymerization reaction are shown in Figures 6 and 7.
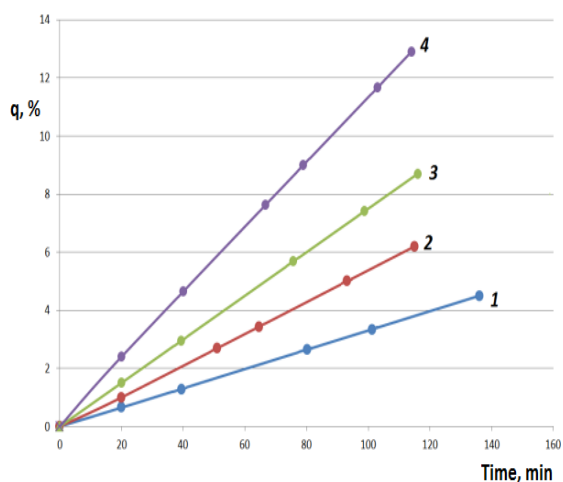
Figure 6. Effect of initiator concentration on polymerization of 1-chlorine-3-piperidine-2-propyl-methacrylate , mol / l 1-1·10⁻³; 2-2·10⁻³; 3-3·10⁻³; 4-5·10⁻³, [M]=0,5 mol / l. T=60 ⁰C, solvent DMFA.
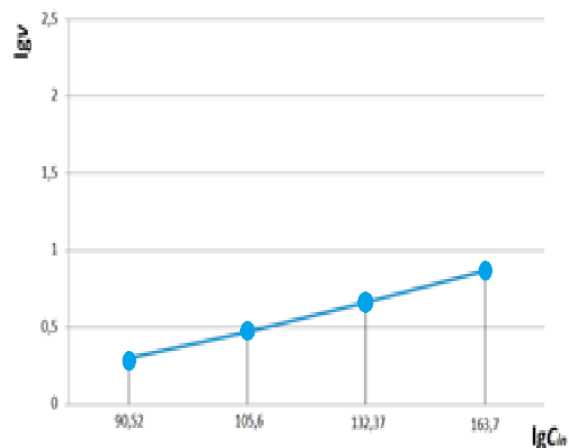
Figure 7. lg V ₚₒₗ = f (lg [M]) dependence graph. [DAK] = 5 · 10⁻³ mol / l , [M]= mol / l : 0,1; 0,2; 0,3; 0,5. T=60 ⁰C, solvent DMFA.

In this process, the initiator concentration (mol / l): $1 \cdot 10^{-3}$; $2 \cdot 10^{-3}$; $3 \cdot 10^{-3}$; $5 \cdot 10^{-3}$; Obtained at values of . Figure 6 based on the threshold lg V_{pol}= f (lg [M]) is the relationship chart, line 7 picture is. The order of the initiator of the polymerization reaction XPPMA was calculated to be 0, 56. This phenomenon suggests that the disruption of the growing chain occurs by a bimolecular mechanism. The effect of temperature in the DMF environment on the polymerization reaction was also studied. The temperature of the polymerization of 1-chlorine-3-piperidine-2-propyl methacrylate varies: : 50; 60; 70; 80 ⁰C, the monomer concentration [M] = 0.5 mol / l was carried out in a solvent DMFA medium. Based on the obtained results, graphs were drawn and the values of activation energies of the process were calculated. The values of these results are given below (Figures 8 and 9).
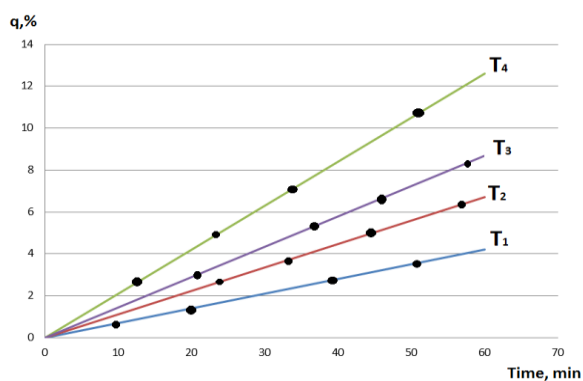

Figure 8. Temperature effect on the polymerization of 1-chlorine-3-piperidine-2-propyl methacrylate , ⁰C: 1-50; 2-60; 3-70; 4-80; [M] = 0.5 mol / l, solvent DMFA.
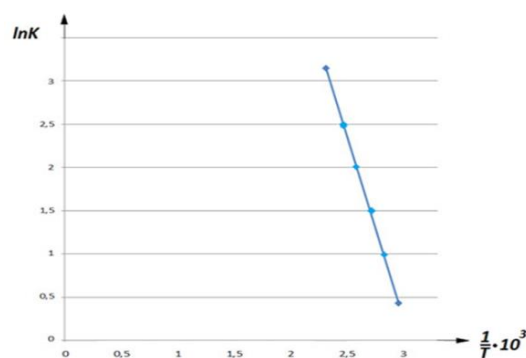
Figure 9. The logarithm of the effective rate constant (ln *K*) of polymerization is the curve of dependence on 1 / T.

According to Figure 8, the activation energy of the polymerization process was calculated to be 59.8 kJ/mol. The results showed that the reaction order for the monomer in the XPPMA polymerization process was 1.5, for the initiator 0.56, and the activation energy of the polymerization process was 59.8 kJ/mol. Based on the results, the reaction order and activation energy values of the polymerization process of XPPA and XPPMA on the monomer and initiator were found.

The results showed that the reaction order for the monomer in the XPPMA polymerization process was 1.5, for the initiator 0.56, and the activation energy of the polymerization process was 59.8 kJ/mol. Thermoanalytic analysis of the synthesized 1-chlorine-3-piperidine-2-propyl methacrylate was performed (Fig. 9).
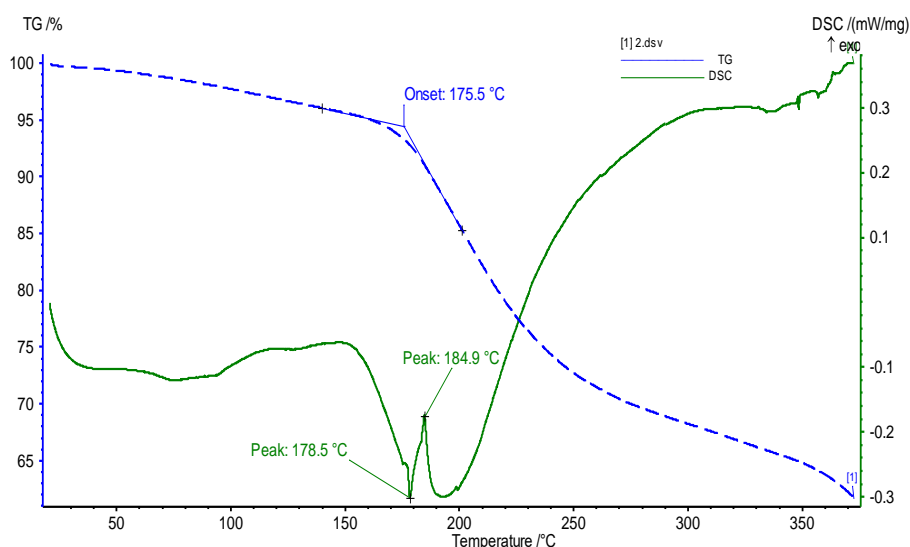

Fig. 9. Thermoanalytic diagram of poly -1-chlorine-3-piperidine-2-propyl methacrylate .

Based on the results obtained, it can be analyzed that the sample did not change its steady state to 175.5 °C. It can be seen that as the temperature rises, the mass of the sample decreases, with two endo- and exothermic peaks in the temperature range of 178.5 and 184.9 °C. The characteristic viscosity of polymers of 1-chlorine-3-piperidine-2-propylacrylate and methacrylates obtained at 40, 60, 70 °C in 0.1 n KCl solution was determined (Fig . 10).
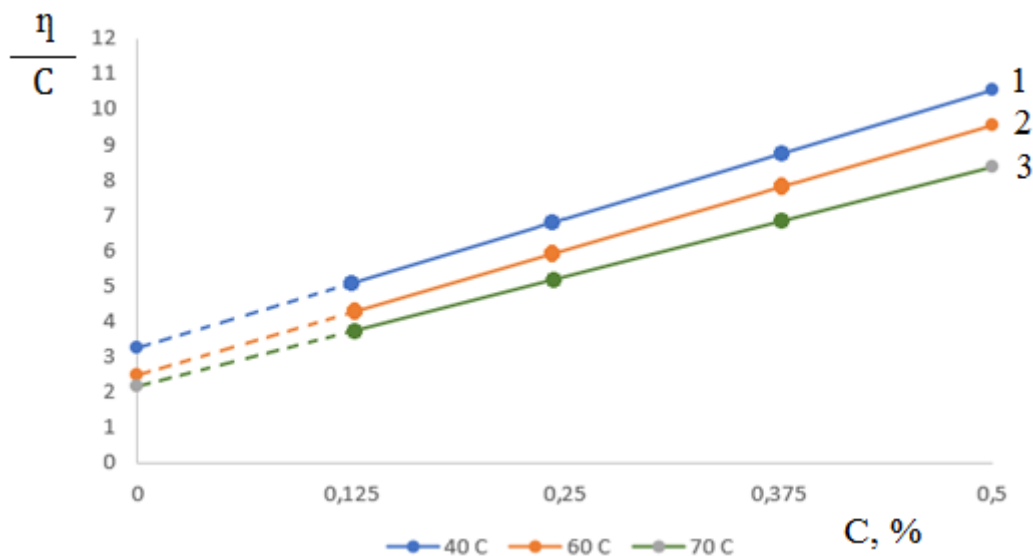

Fig.10 . The effect of temperature on the characteristic viscosity of poly -1-chlorine-3-piperidine-2-propylmethacrylate, °C: 1-40; 2-50; 3-60.

The above results show that the increasing viscosity values of polymers decrease with increasing temperature.

Based on these data, we can say that the characteristic viscosity values of polymers obtained at different temperatures are greater than the viscosity value of the polymer obtained at low temperatures compared to the polymers obtained at high temperatures.

CONCLUSION.

1. An amino alcohol was synthesized on the basis of piperidine and epichlorohydrin. The esterification reaction with the obtained amino alcohol and n acrylic and methacrylic acid was studied.

2. The kinetic laws of radical polymerization reactions of monomer 1-chlorine-3-piperidine-2-propyl- methacrylate were studied. The order of the monomer and initiator of the reaction, the activation energy of the process was calculated.

3 Using viscometric method, the average characteristic viscosity of poly -1-chlorine-3-piperidine-2-propyl- methacrylate was determined.

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