Mechanisms of Formation and Structure Polymer Salts of Dimethylaminoethyl Methacrylate with Heterocyclic Compounds

Ubaydulla Abidjanovich Safaev[1], Zumrat Tairovna Karabaeva[2], Pokiza Xalimovna Rasuleva[3], Raxima Raximdjanovna Isanova[4]

[1,2]Associate Professor, Tashkent State Technical University
[3,4]Head Teacher Tashkent State Technical University

ARTICLE INFO	ABSTRACT
            Corresponding Author: **Ubaydulla Abidjanovich Safaev**	The article presents the results of studies of the main regularities of the polymerization of quaternary monomeric salts of dimethylaminoethylmethacrylate with heterocyclic compounds - N-α-chloromethylbenzoxazolone, N-α-bromomethylmercaptobenzthiazolthione and N-α-chloromethylbenztriazole, determined experimentally the values of the kinetic process parameters. The structure and composition of the newly synthesized monomers and polymers were studied using PMR spectra and elemental composition analysis. The processes of polymerization of monomeric salts based on DMA and heterocyclic compounds were studied, the main kinetic regularities of the reactions were established, and it was shown that the system under study obeys the basic laws of the radical process, which is confirmed by the compilation of a mathematical model of the formal kinetics of the reaction. A mathematical model of radical polymerization was compiled, on the basis of which the ordinal values and activation energy of the reaction were determined and the results were obtained that were adequate with the experimental ones.

INTRODUCTION

The expansion of the field of application of cationic polymers in various areas of the national economy has led to significant interest in their synthesis and the mechanism of formation. Of particular interest are ammonium polymers with functional groups, which have a set of valuable properties.

So, in particular, they are widely used as thermal and light stabilizers, flocculants for wastewater treatment, soil structurators, plant growth stimulators, ion exchangers for the extraction of rare metals, etc. Therefore, the preparation and study of monomeric salts of quaternary derivatives of aminoalkyl methacrylates and polymers based on them are of undoubted theoretical and practical interest.

DISCUSSION

We have synthesized a number of monomers based on aminoalkyl esters of methacrylic acids, in particular, N, N-dimethyl- N, N-dimethylaminoethylmethacrylate (DMA). Derivatives of dialkyl-aminoethyl methacrylates with halogen-containing heterocyclic compounds, as can be seen from the literature data, have not been practically studied.

From this point of view, attention is drawn to the homo- and copolymerization of new monomers - quaternary salts based on DMA with N-α-chloromethylbenzoxazolone (DMA:O), N-α-bromomethylmercaptobenzthiazolthione (DMA:S) and N, α-chloromethylbenzotriazole (DMA:N), polymeric forms of biologically and functionally active substances are more promising than their low-molecular-weight analogues. The macromolecular nature of these substances makes it possible to control their solubility, reduce volatility, and also make them safe for the environment.

There are several ways to obtain derivatives of monomeric quaternary salts of aminoalkyl acrylates [4]. According to the literature, monomers are synthesized at low temperatures. The synthesized monomers are very hygroscopic, so they must be kept in a vacuum at all times. Purification of monomers requires the use of absolutized solvents. Compared with the known monomeric quaternary salts, DMA derivatives with halogen-containing heterocyclic compounds have significant advantages: monomers are synthesized under milder conditions and they are not

hygroscopic. The main characteristics of the synthesized monomeric salts are presented in Table 1

Table 1. Physicochemical indicators of monomers and polymers

| Product	Solvent	Powder color	T_m, ºC
DMA:O	water, ethyl alcohol, DMF, DMS	White	131
poly-DMA:O	the same	the same	136
DMA:S	the same	the same	129
poly-DMA:S	the same	the same	130
DMA:N	water, ethyl alcohol, DMF, DMS	light yellow	133
poly-DMA:N	DMF, DMS	the same	136

The choice of such valuable products as α-chloromethylbenzoxazolone and α-chloromethylbenztriazole as co-components in the synthesis of monomeric quaternary salts is due to their relative availability. Polymers based on them are widely used in the production of medical preparations, as thermal and light stabilizers, activators for vulcanization of rubber compounds, as well as in other technically important areas of the chemical industry.

Monomeric quaternary salts of DMA derivatives with N-α-chloromethyl-benzoxazolone, N-α-bromomethylmercaptobenzthiazolthione and N-α-chloromethylbenzothriazole were synthesized according to the following scheme:
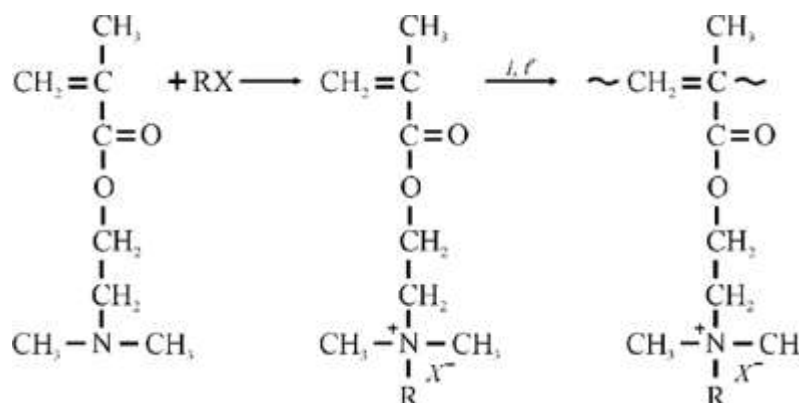
where X - Cl, Br,
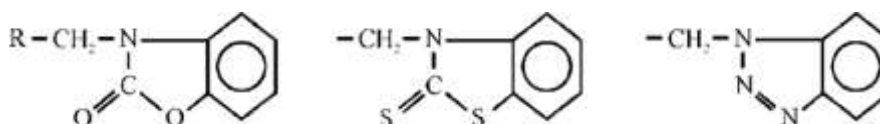
The reactions were carried out at an equimolar ratio of the starting compounds in dioxane at room temperature. The obtained monomers were identified by the method of proton magnetic resonance (PMR), as well as by the results of elemental analysis and physicochemical characteristics.

RESULTS

For the first time, monomeric quaternary salts DMA:O, DMA:S and DMA:N) were synthesized, which are white powders (except for DMA:N), soluble in water and organic solvents, stable during long-term storage, with a density of 7.0-7.5 g / cm³, s T_m = 127-132 ° C.

Heterocyclic compounds with condensed nuclei, containing nitrogen, oxygen and sulfur atoms, possessing thermo-, light-stabilizing and bactericidal properties, are widely used in the production of polymer materials with improved operational properties.

In this aspect, the directed synthesis of polyquaternary salts is promising. For the first time, monomeric quaternary salts of DMA derivatives of interaction with chloromethylbenzoxazolone, N-α-bromomethylmercaptobenztriazole and chloromethylbenz-triazole were synthesized. The structure and composition of the newly synthesized monomers were studied using PMR spectra and analysis of the elemental composition.

Figures 1-3 show the PMR spectra of the synthesized monomers and polymers in a solution of deuterated dimethylformamide (DMF).
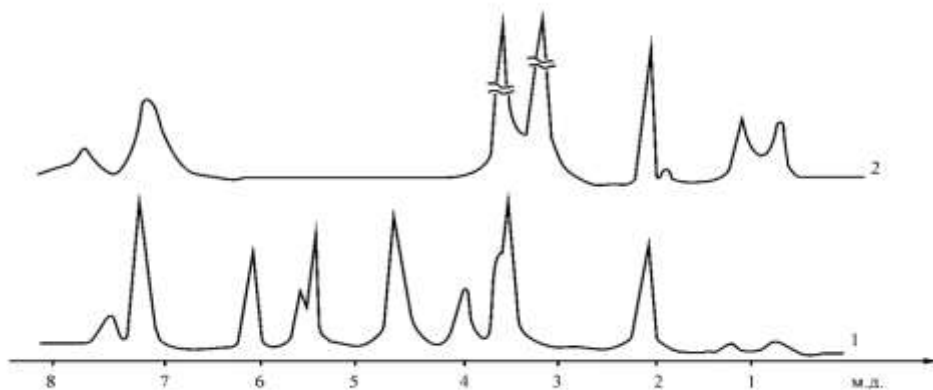
Fig. 1. PMR - spectra of the monomeric quaternary salt DMA:O (1) and poly- DMA:O (2)

The signals of the protons of the C = CH$_3$ group at 6.1 and 5.3 ppm are found in them. Signal at 2.0-2.1 ppm refers to the protons of the methyl group –C – CH$_3$, the signals of the protons of the methylene group –CH$_2$CH$_2$– are traced in the region of 4.1-4.3 ppm. The protons of the methylene group

CH$_2$– linked to the nitrogen atom appear as a multiplet in the region of 5.7 m .d., six-proton signals + (CH$_3$) $_2$ appear as a multiplet in the region of 3.5-3.7 ppm. Intense signal at 7.2 ppm. corresponds to the protons of the aromatic ring.
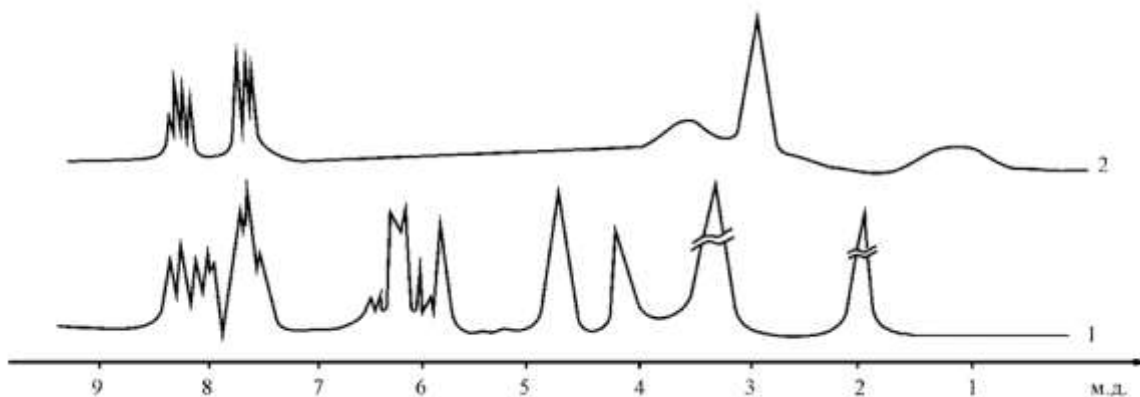

Fig. 2. PMR - spectra of monomeric quaternary salt DMA:S (1) and poly- DMA:S (2)

According to the PMR spectroscopic analysis, the composition and structure of a unit of the resulting polymer completely corresponds to the signal of the protons of the

vinyl and free amino groups, which also indicates the progress of the polymerization process.
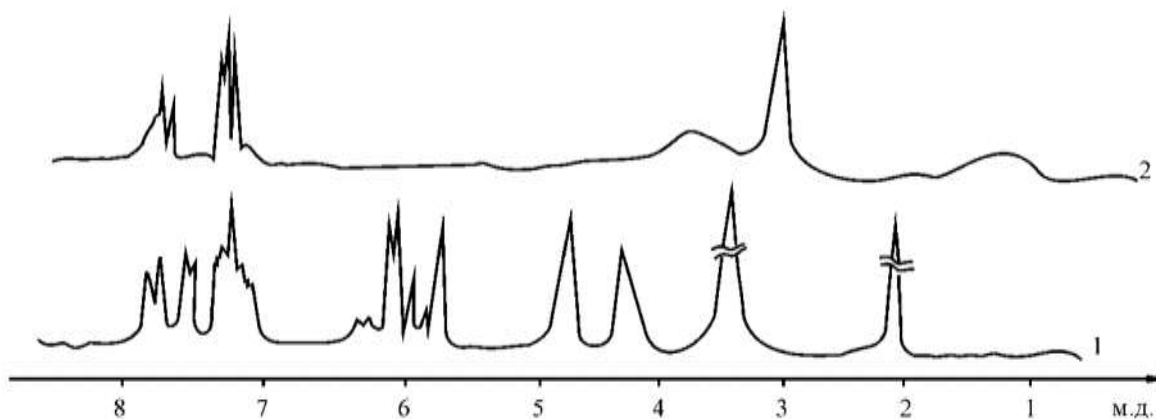

Fig. 3. PMR - spectra of the monomeric quaternary salt DMA:N (1) and poly- DMA:N (2)

Thus, the spectroscopic data confirm the chemical structure of the synthesized monomers.

Table 2 shows the results of elemental analysis of monomeric and polymeric quaternary salts DMA:O, DMA:S and DMA:N.

Table 2. Elemental composition of the synthesized monomeric quaternary salts and polymers based on them

№	Products	Calculated, %					Found,%				
		C	H	N	Br	Cl	C	H	N	Br	Cl
1	DMA:O	56,72	5,65	8,27	-	10,46	56,41	6,12	8,0	-	10,21
2	DMA:O	56,72	5,65	8,27	-	10,46	56,24	5,68	8,53	-	10,00
3	DMA:S	55,47	6,47	17,2	-	26,10	55,60	6,51	16,84	-	24,48
4	DMA:S	55,47	6,47	17,2	-	26,10	55,31	6,20	16,72	-	25,32
5	DMA:N	46,26	4,61	6,74	19,23	-	46,41	4,50	6,70	19,0	-
6	DMA:N	46,26	4,61	6,74	19,23	-	46,16	4,30	6,60	18,8	-

After careful identification of the composition and structure of the synthesized new monomers by PMR and elemental analysis, the possibility of using DMA:O, DMA:S and DMA:N in the polymerization reaction was investigated.

The kinetics of the polymerization process was studied by the dilatometric method in aqueous and organic solutions at 40-60 ° C. The initiators were potassium persulfate (PC), benzoyl peroxide (BP), and dinitrilazobisisbutyric acid (DAA), the concentration of which varied from 0.001 to 0.01 mol / l at a monomer concentration of 0.25-1.5 mol / l.

According to preliminary experiments, monomeric quaternary salts DMA:O, DMA:S and DMA:N in the medium of various solvents and in water in the absence of a radical initiator do not enter the polymerization reaction. The study was carried out at a temperature of 60-70 ° C. Polymerization proceeds only when a radical initiator is added to the system and the process is completely inhibited in the presence of effective inhibitors of radical polymerization, which indicates the radical nature of the process.

The effectiveness of initiators was investigated depending on their nature. It was found that the initial rate of polymerization of the DMA:O quaternary salt in a dimethyl sulfoxide medium in the presence of AIBN is higher than that of PC and PB. In the case of other synthesized monomers (DMA:S and DMA:N), the same pattern is observed. These results are in good agreement with the literature data that during the polymerization of aminoalkyl esters of unsaturated acids and their salts, the most effective initiators are azo compounds [5-8], therefore, in further study of the kinetics of polymerization of quaternary salts DMA:O, DMA:S and DMA:N the process was carried out in the presence of DAA.

The choice of the solvent was based on the need for polymerization under homogeneous conditions (no heterophase). The system must remain homogeneous up to deep conversion, i.e. both the initial monomer and the resulting polymer at these concentrations should completely dissolve in the reaction solutions. Taking these requirements into account, the following solvents were chosen: dimethyl sulfoxide (DMS), dimethylformamide (DMF), ethyl alcohol in aqueous solutions.

It is known [9] that the nature of the solvent significantly affects the kinetics of polymerization of ionizing monomers, and the dependence of the initial rates of polymerization of BODMAC

When studying the reasons for the abnormally high rates of polymerization of the considered ionic monomers in aqueous solutions, along with those noted above, another probability should be noted for all water-soluble monomers (which is known from the literature).

Due to the fact that polymerization proceeds at a higher rate in methanol and the control of the reaction progress gives unreliable results, therefore, DMSO and water were chosen as the solvent.

Investigation of the ordinal regularities of the radical polymerization of quaternary DMA salt derivatives showed that with an increase in the concentration of the initiator and monomer, the rate of the process increases. Kinetic studies of the polymerization of the monomeric quaternary salt of DMA:O were carried out in a wide range of monomer concentrations (0.15-1.0 mol / l) in dimethyl sulfoxide at 60 ° C.

Based on the logarithmic dependence of the polymerization rate on the initiator concentration, the value of "n" was determined for all monomers under study, equal to 0.5.

The found values of "m" indicate a radical mechanism of polymerization of DMA:O, DMA:S and DMA:N with bimolecular chain termination. To determine the order of this reaction with respect to the monomer, it was carried out at various monomer concentrations. The value "m" found on the basis of the logarithmic dependence of the polymerization rate on the monomer concentration is 1.

An important characteristic of the polymerization reaction is the constant of chain transfer to the monomer and initiator. As a rule, the constant of chain transfer to the monomer is found from the dependence of the inverse degree of polymerization on the overall reaction rate (1/P versus

V/[M]^2). These data are obtained by changing either the concentration of the initiator, while leaving the concentration of the monomer unchanged (in our case, the concentration of the monomer was 0.25 mol / l, and the concentration of the initiator was changed in the range 1 · 10-3-0.4 · 10-3 mol / l), or by changing the concentration of the monomer, while leaving the concentration of the initiator constant (1 · 10-3 mol / l = [I] and [M] varied from 0.15 to 0.75 mol / l for DMA:O, from 0 , 21 to 0.66 mol / l for DMA:S and from 0.15 to 0.75 mol / l for DMA:N), the values of which are presented in table 4.

This indicates the presence for this system of a chain transfer constant to the initiator and, as a consequence, an increase in the contribution of this value with an increase in the concentration of the initiator. Therefore, the constant of

chain transfer to the monomer was calculated from the data obtained by changing the monomer concentration. The point corresponding to low monomer concentrations (0.15 mol / l) does not fit into the obtained dependence, which does not contradict the theory of radical polymerization, since immediately becomes more noticeable the transfer of the chain to the solvent and possible trace impurities. A similar picture can be observed during the polymerization of the DMA:O monomer.

It can be seen from the data obtained that for DMA:O at low initiator concentrations, the dependence is linear, and with an increase in the initiator concentration to 4 × 10-3 mol / L, a sharp increase in the inverse degree of polymerization is observed.

Table 4. Kinetic parameters of the polymerization rate monomeric quaternary salts depending on concentration monomer and initiator (T = 60 ℃)

Monomer	Monomer concentration, mol / l	Initiator concentration, mol / l · 10^{-3}	V · 10^5 mol / l · s	[η], dl / g
DMA:O	0,15	1	1,1	0,71
	0,25	1	3,8	1,74
	0,50	1	7,6	2,4
	0,75	1	12,0	2,6
	0,25	2	5,2	1,3
	0,25	3	7,0	1,0
	0,25	4	8,2	0,8
DMA:S	0,21	1	3,6	0,9
	0,21	2	4,5	0,7
	0,21	3	5,8	0,6
	0,44	1	8,8	1,86
	0,66	1	13,0	2,26
DMA:N	0,15	1	1,0	0,85
	0,25	1	3,1	2,2
	0,25	2	6,0	1,6
	0,25	3	7,2	1,25
	0,25	4	8,2	1,1
	0,5	1	7,0	2,6
	0,75	1	13,0	2,7

In the case of DMA:S, we were able to calculate the chain transfer constant from both dependences. In all cases, the constant of chain transfer to monomer C_M was calculated by the formula:

$$\frac{1}{p} = \frac{K_0}{K_p^2} \cdot \frac{V}{[M]^2} + C_M + C_J \frac{[I]}{[M]}$$

where:

P-degree of polymerization;

V - the total polymerization rate;

[M] - the concentration of the monomer;

[I] - the concentration of the initiator;

C_M -constant of chain transfer to monomer;

C_J - the constant of the chain transfer to the initiator.

In the case of a linear dependence of 1 / P on V / [M]^2, the last term of the equation can be neglected, then the segment cut off by the linear part of the curves determines the value of Cm, from the slopes of the graphs of dependences, one can determine K$_o$ / K$_p$^{2}. The degree of polymerization was determined from molecular weights of polymers found by the Mark-Kuhn-Houwink formula derived for DMA:O in this work. The molecular weights of the other two polymers were

also calculated from this formula using K and α derived for DMA:O. The calculation data are shown in Table 9.

From the graphical dependencies, the CMs were found for three different monomers during the polymerization reaction at 60 ° C, they turned out to be equal: for DMA:O - 0.34 · 10^{-2}; for DMA:S - 0.26 · 10^{-2} and for DMA:N - 0.4 · $10^{-2} \div 0.5 \cdot 10^{-2}$. Thus, we can say that for all three monomers the found values of the chain transfer constants are very close to each other, which should be expected, taking into account the structural formula of the monomers under discussion.

An increase in the reaction rate with increasing temperature was found. Using the Arrhenius equation, the total activation energy was determined, which for DMA:O, DMA:S and DMA:N corresponds to 68.16; 67.12 and 61.44 kcal / mol.

Thus, the initial polymerization rate of the quaternary salts DMA:O, DMA:S and DMA:N can be described within the framework of the well-known equation of radical polymerization:

$$V_{pol} = K[M]^{1,0} \cdot [I]^{0,5}$$

To increase the reliability of the information obtained on the kinetic constants of the BODMAC polymerization reaction, the initial results were mathematically processed by the method of statistical analysis of the experiment [12].

The activation energy and the order of the reaction for the starting components were determined by the dilatometric method. For this, kinetic curves were obtained for the time dependence of the degree of conversion of the starting monomers into polymers at various temperatures and concentrations of the starting monomers.

The kinetic equation for the rate of polymerization of DMA:O in the presence of DAA is described as

$$V_{pol} = K [DAA]^n [DMA:O]^m \qquad (1)$$

Taking into account that for Arrhenius systems $K = A\, e^{(-E/RT)}$ equation (1) can be reduced to the form:

$$V_{pol} = A [DAA]^n [DMA:O]^m \cdot e^{(-E/RT)} \qquad (2),$$

where A is a pre-exponential factor; R - gas constant; T is the temperature; E is the activation energy.

To determine the constants A, n, m, E equation (2) with a minimum number of experiments using the method of mathematical planning of experiments.

The kinetic equation for the polymerization of the monomeric quaternary salt $DMA:O$ in the presence of DAA is written as follows:

$$Vpol = 1.17 \cdot 10^{-3}[DAA]^{0.6} \cdot [DMA:O]^{1.1} \cdot e^{-\frac{65.6}{PT}}$$

Table 5 shows the results of mathematical processing of the obtained kinetic studies, as well as those determined by the graphical method.

Table 5. The values of the activation energy and the order of the reaction, found graphically and calculated

Order by DMA: O		Order by DAA		Activation energy, E, kJ / mol		Experimental inaccuracy
graphical	calculated	graphical	calculated	graphical	calculated	
1,0	1,1	0,5	0,6	67,12	65,6	5,3 · 10^{-4}

Thus, with the help of the mathematical theory of experiment planning, a mathematical model of radical polymerization was compiled, on the basis of which the optimal process conditions were determined and the results were obtained that were adequate with the experimental ones.

It was of interest to study the effect of the degree of ionization on the kinetics of polymerization of the monomeric quaternary salt DMA: O. It is known that the behavior of monomers capable of ionization during polymerization in aqueous solutions, in comparison with nonionic vinyl monomers, is mainly due to the fact that they, like the corresponding units of polymer chains, in specified pH ranges exist in both ionized and non-ionized condition. It should be noted that during the polymerization of ionizable monomers in aqueous solutions, the polymerized particles must be sensitive to the nature of the reaction medium, i.e. to pH, ionic strength and degree of ionization of monomers. We have investigated the kinetics of radical polymerization of a monomer salt based on DMA:O in aqueous solutions, and also studied the effect of pH and ionic strength on the direction of elementary reactions of the polymerization process.

To obtain more detailed information on the mechanism of the radical polymerization process, the effect of pH and ionic strength on the kinetics of the reaction of the monomeric quaternary DMA salt with chloromethylbenzoxazolone was studied.

The kinetics of radical polymerization of the monomeric quaternary salt of DMA:O in aqueous solutions was studied by the dilatometric method in a wide range of pH values (1-7), controlled by the addition of NaOH or H_2SO_4, at conversions not exceeding 10%. Preparation of reaction solutions and filling of dilatometers was carried out in a closed environment (10-3-10-4 mm Hg) to obtain reproducible results, monomers and other components of the reaction solutions were thoroughly purified. The polymerization of the DMA:O monomer was initiated by the thermal decomposition of DAA. It was found that, in the

absence of an initiator, the reaction at the studied temperatures does not proceed in the entire consecutive range of pH values. Under the same conditions, for the DMA:O monomer, the polymerization rate is half the order of the initiator concentration, which indicates a bimolecular chain termination mechanism. The reaction is completely inhibited by an effective radical inhibitor, a stable iminooxyl radical, and does not proceed in the absence of a radical initiator. The reaction rate is of the first order of magnitude in monomer concentration.

Figure 5 shows the dependence of the rate of polymerization at different pH values of the medium, established by the addition of H_2SO_4, on the concentration of low molecular weight electrolyte (KCl). The figure shows that at pH = 1-7, the polymerization rate does not change sharply.

It is important to note that the addition of KCl at pH 1-7 does not affect the initial polymerization rate. The absence of a kinetic effect is apparently due to the formation of an intramolecular complex.
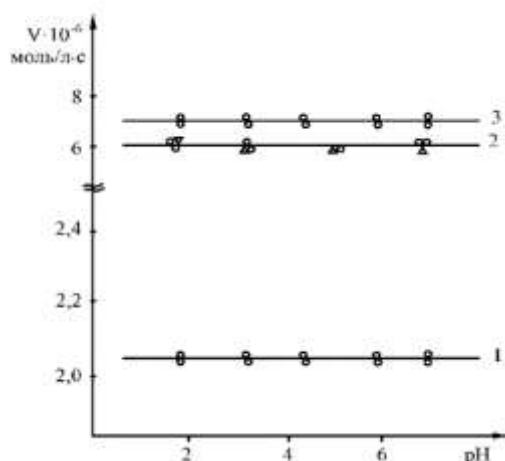

Fig. 5. Dependence of the polymerization rate of DMA:O (1), DMA:S (2) and DMA:N (3) on the pH values established by the addition of H_2SO_4 and low-molecular salt KCl, [M] = 0.25 mol / l, [DAA] = 1 · 10-3 mol / l, T = 60 ° C, [KCl] = 1.0 mol / l

It is known from the relevant literature that at pH 2-6 the rate of polymerization of DMA is practically independent of the reaction solutions.

In the system under study, the resulting polymer is a strong base, and in the specified pH range, the polymer chains are completely ionized. In this regard, an increase in the ionic strength of the solution in the acidic region, it would seem, should contribute to an increase in the rate of polymerization in accordance with the mechanism of ion pairs. However, no change in the reaction rate was found. pH. An increase in the ionic strength of the reaction solution at a fixed pH does not affect the polymerization rate, i.e. the mechanism of ion pairs does not seem to manifest itself.

An increase in the concentration of counterions does not affect the overall kinetics of the polymerization process, i.e. does not change the relative contribution of electrostatic interactions, reacting charged particles in the acts of chain growth.

It is assumed that relatively hydrophobic polycations are characterized by an increased ability to bind low-molecular-weight anions even at low ionic strengths and thereby neutralize the effective positive charge at the ends of growing chains, even at those pH and ionic strength values at which the concentration of anions in solution is very low.

The initiation rate was determined by the inhibition method in the presence of a radical inhibitor, 2,2,6,6-tetramethylpiperidyl-1-oxide (TMPO). Figure 6 shows the dependence of the yield of the polyquaternary salt DMA:O, DMA:S and DMA:N on the polymerization time at various inhibitor concentrations. It can be seen that the rate of polymerization of monomers after the consumption of the inhibitor coincides with the rate of the process without the inhibitor.
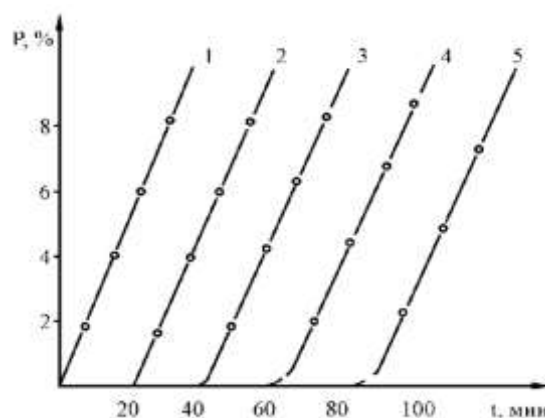

Fig. 6. Dependence of the degree of conversion on the concentration of TMPO at T = 60 ° C; DMS; [DMA:O] = 0.25 mol / L; [DAA] = 1 · 10-3 mol / l; [TMPO] mol / l: 1 - 0; 2 – 1,2 10-4; 3 – 2,4 10-4; 4 – 3,6 · 10-4; 5 – 4,8 10-4

The radical nature of the DMA:O salt polymerization was investigated by the method of radical "trap" in the presence of TMPO using EPR (Figure 7, curve 1). It can be seen from the figure that TMPO in ethanol gives a spectrum of three lines, the intensity of the spectral lines did not change for 6 hours.

When TMPO is added to the DMA:O + DAA system (in the DMS medium, the resolution of the magnetic field is very high, and the intensity of the spectral lines is very weak), the intensity of the spectral lines decreases (Figure 7, curve 2). This is explained by a decrease in the concentration of TMPO in the system due to their binding by DAA radicals, which is an additional confirmation of the radical character of DMA:O polymerization.
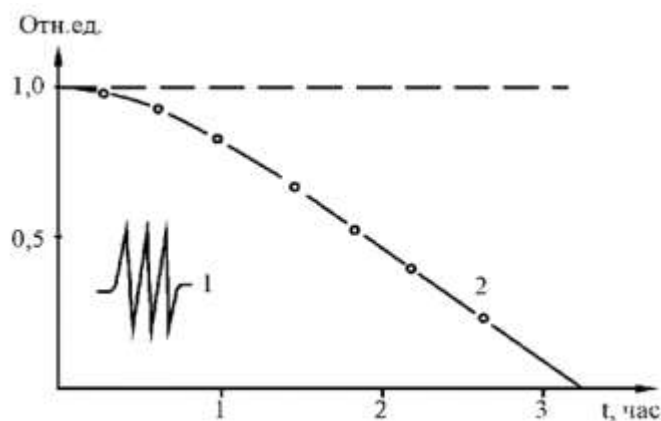
Fig. 7. Change in the intensity of the EPR signal of TMPO in the presence (1) and absence (2) of a monomer and an initiator: [DAA] = 1 · 10-3 mol / l; [TMPO] = 1 · 10-4 mol / l; [DMA:O] = 0,25 mol / l

To determine the initiation rate (Win), polymerization was carried out in the presence of TMPO at various concentrations (Table 6).

When a certain amount of inhibitor is introduced, the proportionality of the induction period is observed; after the end of the induction period, the polymerization rate coincides with the polymerization rate without the inhibitor.

The initiation rate was calculated by the formula:

$$Win = \frac{[Inh]}{\tau}$$

where, Inh - is the amount of injected inhibitor, mol / l;
τ - is the duration of the induction period, s

Table 6. Calculation of the rate of initiation of the polymerization reaction DMA:O, DMA:S, DMA:N at T = 60 ° C, [DAA] = 10^{-3} mol / l

Monomer	[M], mol / l	[Inh], mol / l	W_{in}, mol / l·s	K_0/K_p^2
DMA:O	0,25	$1,2 \cdot 10^{-4}$ $2,4 \cdot 10^{-4}$ $3,6 \cdot 10^{-4}$ $4,8 \cdot 10^{-4}$	$1 \cdot 10^{-7}$	4,4
DMA:S	0,21	$1,2 \cdot 10^{-4}$ $2,4 \cdot 10^{-4}$ $3,6 \cdot 10^{-4}$ $4,8 \cdot 10^{-4}$	$1,58 \cdot 10^{-7}$	5,38
DMA:N	0,25	$1,2 \cdot 10^{-4}$ $2,4 \cdot 10^{-4}$ $3,6 \cdot 10^{-4}$ $4,8 \cdot 10^{-4}$	$0,9 \cdot 10^{-7}$	5,85

Knowing the value of the initiation rate from the basic kinetic equation of radical polymerization, it is possible to determine the ratio $K_p / K_o^{0.5}$, which in the studied conditions was 0.35 s^{-1}.

$$V_n = \frac{K_p}{K_0^{0,5}} \cdot W_{uн}^{0,5}[M]$$

The found values from two series of kinetic studies are in full agreement with each other. In addition to the fact that the three different monomers: DMA:O, DMA:S and DMA:N, the values of this value are close to each other.

CONCLUSION

Thus, the processes of polymerization of monomeric salts based on DMA and heterocyclic compounds were investigated, the main kinetic regularities of the reactions were established, and it was shown that the system under study obeys the basic laws of the radical process, which is confirmed by the compilation of a mathematical model of the formal kinetics of the reaction. On the basis of the revealed equation, the optimal conditions of the process are determined and the results are obtained that are adequate with the experimental ones.

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