

Peculiarities of the Interaction of Dimethylaminoethyl Methacrylate with Alkyl Esters of Halogenacetic Acids

Zumrat Tairovna Karabaeva, Ubaidullah Abidjanovich Safayev, Mukarram Majidovna Aripova, Pokiza Xalimovna Rasuleva, Nargiza Tulkunovna Raxmatullayeva

Abstract—The article presents the results of kinetic studies of polymerization of monomer salts forming at interaction of dimethylaminoethyl methacrylate with a number of esters of chloroacetic acid and also shows the course of spontaneous polymerization in the environment of organic solvents simultaneously by formation of ammonium salt. It was found out that the reaction of quaternization and further spontaneous polymerization take place both in the presence of the solvent and in the mixture of initial components.

Keywords: Dimethylaminoethyl methacrylate, ethyl chloroacetic acid ester, quaternization, dilatometric method, monomer salt, polymerization.

1. INTRODUCTION

It is known that at interaction of some monomer systems forming ammonium groups, instead of formation of monomeric salts the subsequent spontaneous polymerization occurs [1-5]. In this case, synthetic polymers are formed, which are of practical value because their synthesis by other methods is a complex task.

Previously, the results of the study of such systems with the participation of some halogen-containing monomers in interaction with tertiary amines were reported [6-10].

We have established that a similar process may occur in the interaction of monomeric amine - dimethylaminoethyl methacrylate - with halogen-containing compounds - esters of halogen acetic acids.

For systematic research of radical polymerization processes monomer salts of the next series based on acrylic monomer – dimethylaminoethylmethacrylate (DMA) were selected in its interaction with:

- ethyl ether of chloroacetic acid (EEA);
- propyl ether of chloroacetic acid (PEA);
- allyl ether of chloroacetic acid (AEA);
- hexyl ether of chloroacetic acid (HEA);
- decile ester of chloroacetic acid (DEA).

The monomeric and polymeric salts obtained on their basis were identified by spectroscopic methods and by the results

of elemental analysis. The elemental composition of some monomer salts and their polymers is presented in Table 1.

To prove the formation of monomeric quaternary salt DMA with EEA and its polymer, the PMR spectra were taken (Fig. 1).

At the same time, the following signal attribution was made in the spectra: triplet in the region of 0.4-0.9 m.u. caused by protons of the end CH₃ group, region 1.1-1.7 m.u. - protons CH₃=N-CH₃, 4.5 m.u. - protons CH₂-COO; 6.3-6.8 m.u. - protons of the vanilla group CH₂, 4.7 m.u. - protons of methylene group with unbalanced nitrogen electrons CH₂-N.

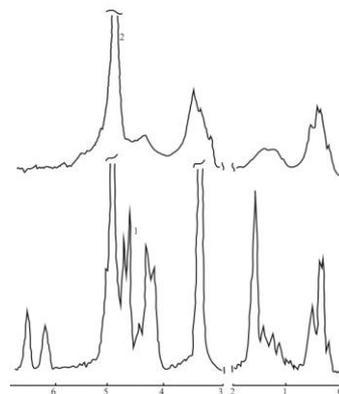
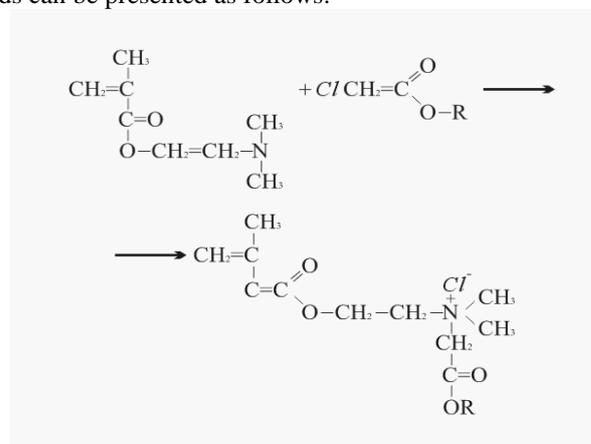


Figure 1 - PMR of DMA spectrum with EEA (1) and its polymer (2)

Based on the data of spectroscopic researches and elemental analysis the scheme of formation of monomeric quaternary salts of DMA with alkyl ethers of chloroacetic acids can be presented as follows:



Where, - C₂H₅, -C₃H₇, -C₃H₅, -C₆H₁₃, -C₁₀H₂₁

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Table 1 - Elemental composition of monomer salts and their polymers

Connection	Calculated, %				Found, %			
	C	H	N	Cl	C	H	N	Cl
DMA · EEA	51,6	7,81	5,01	12,7	51,1	7,89	5,21	12,5
polyDMA · EEA	51,6	7,81	5,01	12,7	51,3	7,87	5,20	12,3
DMA · DEA	61,3	9,70	3,58	9,1	61,2	9,61	3,51	8,9
polyDMA · DEA	61,3	9,70	3,58	9,1	61,0	9,59	3,53	9,0

To identify the most common polymerization patterns of amino alkyl acrylates and their derivatives, it is necessary to conduct kinetic studies of the radical polymerization reaction of these monomers.

Polymerization kinetics was measured by dilatometric method in water, dimethyl sulfoxide (DMSO), dimethylformamide (DMFA) and ethyl alcohol.

Radical polymerization of monomeric quaternary salts results in the formation of polymers corresponding to the composition and structure of the initial monomers.

It has been found that for all synthesized monomers in these solvents the first order of polymerization rate by monomer concentration and half the rate by initiator concentration are observed, which indicates the bimolecular nature of chain breakage.

Table 2 presents the kinetic polymerization regularities in different solvents of monomeric quaternary salts of DMA derivatives.

Table 2 - Polymerization rate of monomeric quaternary salts in different media (T=60°C, [M] = 0,25 mol/l, [DAA] = 1·10³ mol/l)

Monomeric salt	Reaction environment	V · 10 ⁵ mol/l·s	[η], dl/g in 1 _{normal} NaCl
DMA · EEA	water	6,0	1,95
	DMSO	2,8	
	DMFA	1,9	
	ethanol	2,2	0,45
DMA · PEA	water	5,0	1,55
	DMSO	2,1	
	DMFA	1,3	
	ethanol	2,0	
DMA · AEA	water	4,9	1,98
	DMSO	2,8	
	DMFA	1,9	
	ethanol	2,0	0,50
DMA · HEA	water	4,0	2,10
	DMSO	2,6	0,60
	DMFA	1,7	
	ethanol	1,8	
DMA · DEA	water	3,6	2,40
	DMSO	1,5	
	DMFA	1,6	
	ethanol	1,3	0,61

Polymerization of quaternary salt DMA · EEA was carried out in the environment of organic solvents in the presence of the initiator of radial polymerization of dinitrileasobisolic acid (DAA) at a temperature range of 30-50 °C. At the same time, a water-soluble cationic polymer with a sufficiently

high molecular weight is formed. Figures 2 and 3 show that with increasing concentration of monomer salt the characteristic viscosity of formed polymers increases, and with increasing concentration of initiator decreases.

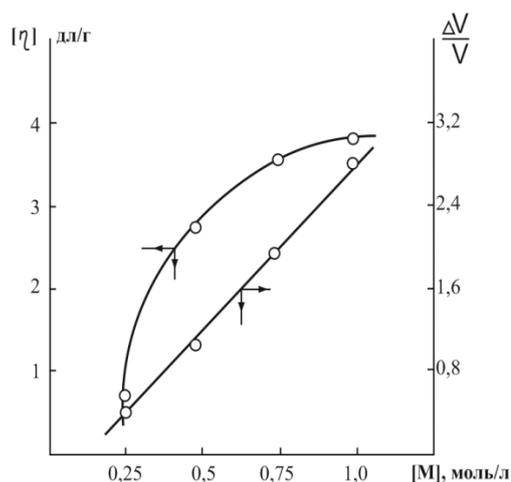


Figure 2 - Dependence of DMA · EEA polymerization rate and characteristic viscosity on monomer concentration, [DAA] = 0.01 mol/l

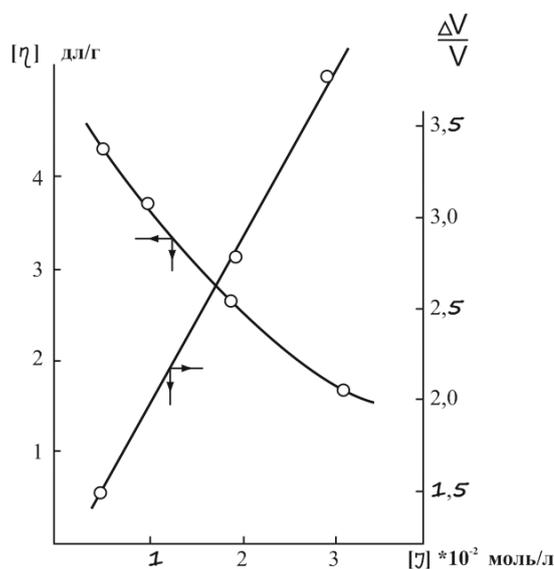


Figure 3 - Dependence of DMA · EEA polymerization rate and characteristic viscosity on initiator concentration, [M] = 0.75 mol/l

An overestimated monomer reaction order value indicates the participation of some part of monomeric quaternary salt except for chain growth reaction and initiation acts. From the received data it is possible to assume about formation in the conditions of polymerization of a molecular complex with transfer of a charge between monomer salt and initiator of DAA which decay leads to formation of the active centers of polymerization by quaternary salt and DAA which decay leads to formation of the active centers of polymerization.

It should be noted that at these temperatures the thermal decomposition of the selected initiator does not occur. In the absence of an initiator in the system under study, polymerization does not take place, i.e. there is no "dark reaction".

Thus, the results of experimental studies on the kinetics of reactions suggests that the interaction of monomeric quaternary salts DMA· EEA and DMA· DEA with the initiator produces initiating radicals that allow the radical polymerization of quaternary salts in the polar organic solvent at relatively low temperatures by the donor-acceptor mechanism. It should be noted that with the increase in the lateral radical length of monomeric salts DMA· EEA and DMA· DEA, the polymerization rate fits.

Spontaneous polymerization in the system of dimethylaminoethyl methacrylate with ethyl ether of chloroacetic acid in the environment of organic solvents is observed simultaneously in the formation of ammonium salt, i.e. reaction of salt formation (quaternization). It was found out that the reaction of quaternization and further spontaneous polymerization take place both in the presence of the solvent and in the mixture of initial components, i.e. when mixing monomeric amine and halogen-containing compound. However, in this case, the reaction is heterogeneous, since the resulting polymer is insoluble in a liquid mixture of reagents. For this reason, in the further detailed study only the polymerization reactions in plants, occurring in homogeneous conditions, were studied.

In DMA solutions in various organic solvents (ethyl alcohol, DMSO, DMFA, etc.) in the presence of the radium of halogen-containing compounds in the region of 10-60°C, with noticeable speeds there is a spontaneous homogeneous reaction that accompanies the reaction of salt formation and leads to the formation of a polymer. During the process there is an increase in the viscosity of the reaction solution, and the resulting polymer consists of links corresponding to the composition and structure of monomeric quaternary salt.

The reaction of quaternization of unsaturated amine by halide alkyl with formation of monomeric quaternary salt takes place in different conditions without expressed induction period. At the same time, it is established that appreciable quantities of polymer are found out only after the enough quantity of monomeric quaternary salt has already formed in the system. Considering these circumstances, the detailed study of the initial stage of quaternization reaction in conditions when the associated formation of polymer in the reaction system can be neglected.

Study of kinetic regularities of DMA quaternization reaction by ethyl chloroacetic acid ether in different solvents (ethyl alcohol, DMFA, DMSO) showed that according to general regularities of quaternization reaction:

- the speed of the studied reaction increases with the

increase of solvent polarity, i.e. increases in the abovementioned number of solvents;

- speed of reaction decreases at decrease in mobility of halogen, i.e. at replacement of bromine by chlorine;
- the reaction rate decreases with increasing the length of carbon-hydrogen radical in the esters of chloroacetic acid.

In view of the received results for the further systematic studying the reaction between DMA and ethyl ether of chloroacetic acid in ethyl alcohol was chosen.

Kinetics of quaternization reaction in ethanol was measured by two methods - dilatometric method. Values of the rate constant of salt formation reaction for this system, obtained by different methods, in all cases coincided well. It is shown that the quaternization reaction is characterized by the first orders of velocity in terms of initial reagent concentrations.

It was also shown that the velocity constant of the studied quaternization reaction is practically constant in the region of relatively small initial concentrations of reagents [DMA] = [EEA]=0,25-2,5 mol/l. At higher concentrations of reagents, an increase in the value of K_m was found, which is a consequence of changes in the polarity of the reaction medium compared with the polarity of the solvent - ethanol. The obtained values of the salt formation reaction rate constant are presented in Table 2.

By changing the value in the temperature range of 20-50 °C was determined the value of activation energy of the reaction of DMA· EEA quaternization in ethanol, which was equal to 19.6 kkal/mol. Thus, the following conditions were chosen for the systematic study of the sponsored polymerization: medium - ethanol, temperature interval of 30-50°C and concentration interval from 1.0 to 2.0 mol/l.

Table 2 - Values of the salt formation reaction rate constant for the DMA· EEA-ethanol system

Initial reagent concentrations DMA· EEA, mol/l	Temperature, °C	$V_C \cdot 10^5$ mol/l·s	$K_C \cdot 10^5$
1,0:1,0	30	1,46	1,34
2,0:2,0	30	4,88	1,42
1,0:1,0	40	3,67	3,68
2,0:2,0	40	7,80	3,85
1,0:1,0	50	8,34	5,55
2,0:2,0	50	12,00	6,34

Thus, it is shown that in the absence of monomeric quaternary salt in initial reaction solutions at the initial moment of time, the studied spontaneous polymerization leading to the formation of poly-quaternary salt begins not simultaneously with the reaction of quaternization but becomes noticeable only after a period of time sufficient for the formation of a certain amount of monomeric quaternary salt in the system.

However, the question arises whether spontaneous polymerization will begin simultaneously with the quaternization reaction if a monomeric quaternary salt is introduced into the initial reaction system.



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Experiments have shown that by adding to the initial solutions ($T=50^{\circ}\text{C}$, $[\text{DMA}] = [\text{EEA}] = 1 \text{ mol/l}$) the preliminarily obtained quaternary salt in the concentration of 0.3 mol/l polymerization begins without an induction period. It is important to note that the initial rate of reaction of salt formation at introduction of monomeric quaternary salt does not practically change. Considering this fact, and also knowing the value of the salt formation reaction rate, therefore, corresponding to the value of salt studied conditions, the rates of spontaneous polymerization in the systems, the initial solutions of which introduced the previously obtained monomeric quaternary salt, were determined. Polymerization kinetics is measured at the initial part of the kinetic curve, because this part corresponds to both the linear dependence of the salt formation rate and the rate of polymerization on the duration of the reaction.

The value of the polymerization rate is determined by the difference between the total change in volume and the change in volume of the corresponding reaction of salt formation for a fixed period of time:

$$\Delta V_{\text{floor}} = \Delta V_{\text{sum}} - \Delta V_{\text{sol}}$$

Based on a certain value of specific contraction at polymerization of monomeric quaternary salt, the value of polymerization rate is calculated.

The totality of results of kinetic measurements is reduced to the following:

- spontaneous polymerization occurs only in the presence of both reagents of salt formation reaction - DMA, EEA and monomeric quaternary salt - DMA·EEA (formed as a result of quaternization reaction or obtained and injected into the initial reaction solutions);
- The rate of spontaneous polymerization has the second order of concentration of quaternary salt introduced in advance;
- the rate of spontaneous reaction at a fixed concentration of pre-introduced monomeric quaternary salt has the first order of concentration of each of the reagents of salt formation reaction, the interaction of which produces an additional amount of quaternary monomeric salt in the binary system;
- the rate of spontaneous reaction does not change with the introduction of strong radical inhibitors into the reaction system (2,2,6,6-tetramethylpiperidyl-1-oxyl);

Introduction of styrene and acrylonitrile as comonomers into the reaction system does not lead to the formation of copolymers. In all cases a homopolymer is formed from quaternary monomeric salt.

The last two circumstances obviously testify to the non-radical nature of active growth centers of chains responsible for spontaneous polymerization.

Values of characteristic viscosity of the polymers received as a result of spontaneous polymerization in different conditions were measured, for which they varied:

- 1) initial concentrations of reaction reagents [DMA] and [EEA];
- 2) concentration of monomeric quaternary salt in initial solutions [DMA·EEA];
- 3) duration of polymerization.

The data obtained are given in Table 3.

The influence of additives of proton-donor compounds, which used acetic acid, on the molecular mass of the resulting polymer was also studied. Adding a relatively small amount of acetic acid (1% of the amount of monomeric quaternary salt) leads to a sharp drop in the value $[\eta]$, i.e. the molecular weight of the resulting polymer: $[\eta]$ decreases from 1,5 to 0,12.

Table 3 - Spontaneous polymerization of DMA in interaction with EEA (environment - ethanol, $T=40^{\circ}\text{C}$)

Initial reagent concentrations, mol/l			Duration, min.	Conversion degree, %	$[\eta]$ in I_{normal} water solution NaCl, 25°C
[DMA]	[EEA]	[DMA·EEA]			
1,0	1,0	0,5	15	5,2	1,90
			30	7,2	2,15
			45	10,0	2,20
			60	12,5	2,30
1,0	1,0	1,0	15	5,5	2,15
			30	7,3	2,30
			45	13,7	2,35
			60	17,0	2,40
0,5	0,5	1,0	15	7,0	2,23
			30	15,0	2,30
			45	18,8	2,39
			60	20,50	2,46

The following conclusions were drawn from the data obtained:

- the molecular weight of the polymer during polymerization does not practically change, i.e. does not depend on the degree of conversion;
- polymer molecular weight at the given initial concentration of monomer salt does not depend on the concentration of reagents in the reaction of salt formation, i.e. on the concentration of DMA and EEA.

The molecular mass of the resulting polymer increases with the increase in the initial concentration of monomeric quaternary salt in the reaction system, all other conditions being equal;

Addition of very small amounts of acetic acid to the reaction solutions in the conditions of spontaneous polymerization leads to a sharp drop in the value of molecular mass of the resulting polymer, which also indicates the nonradical nature of the active centers of growing chains and allows us to assume the anionic nature of initiation.

2. RESULTS AND DISCUSSION

Thus, the kinetic features of radical polymerization of a few monomeric quaternary salts on the basis of dimethylaminoethylmethacrylate have been studied and some regularities of the reaction of polymerization of these monomers in different solvents have been investigated. It is important to note that this, in our opinion, has a significant



practical significance, that for all monomers the polymerization rate in water and molecular masses of the resulting polymers are much higher than in organic solvents.

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