

Features of the Process for Obtaining Polymer Quaternary Ammonium Salts

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ABSTRACT

This article presents the results of the synthesis of quaternary ammonium monomers by quaternization of N, N-dimethylaminoethyl methacrylate ethyl and isopropyl iodide. The structure of the synthesized monomers was identified by Infrared and Proton Nuclear Magnetic Resonance spectroscopy and elemental analysis. The possibility of carrying out radical polymerization of the synthesized monomeric quaternary salts at low temperatures using dinitrilazobisisobutyric acid as an initiator has been shown. The influence of various factors on the polymerization process has been studied: the nature of solvents, monomer concentration, initiator and temperature. The order of the reaction with respect to the monomer, initiator, and the total activation energy of the polymerization process, as well as the ratio of the rate constants for the growth and termination of chains, have been determined. The formation of donor-acceptor complexes between monomeric quaternary salts and the initiator under the conditions of the polymerization reaction has been shown by Infrared and Ultraviolet spectroscopy. The composition of the complex was identified, and the equilibrium constants and thermodynamic parameters of the complex reaction were calculated.

Key words: synthesis, quaternary salt, initiator, radical polymerization, donor-acceptor complex.

Introduction

Among the large class of carbo-chain functionally active monomers and polymers based on them, an important place is occupied by polymeric quaternary salts, which is due to both the specific features of the reactions of formation of polymers of this group and their various useful properties. Poly (N, N-dimethylaminoethyl methacrylate) quaternary salts have been the subject of research attention for a long time. They dissolve in water solutions and have a good antimicrobial effect [1-4], are used as flocculants [5], a carrier for medicine [6], etc.

In recent years, scientists have paid much attention to the development of polymeric quaternary salts with antibacterial activity [7-13].

An analysis of the results of numerous studies on the polymerization of quaternary salts shows that the studies were mainly carried out by the method of free-radical polymerization, i.e. with thermal decomposition of the initiator [14]. One of the ways of directed synthesis of carbo-chain functional-active polymers is complex-radical polymerization at relatively low temperature, initiated by the donor-acceptor interaction of the polymerizing monomer with the initiator of radical polymerization, which leads to a decrease in the activation energy required for the process and prevents the occurrence of undesirable side reactions.

The aim of this work is to study the synthesis of polymeric quaternary ammonium salts at moderate temperatures.

Experimental research

Materials

DMAEMA was distilled under reduced pressure to remove the inhibitor prior to use. Hydroquinone and dinitrilazobisisobutyric acid (DBA) were purified by recrystallization. Ethyl and isopropyl iodides, acetone, ethanol, dimethylformamide, dimethyl sulfoxide and other solvents were purchased from the Guangzhou Chemical Reagents Plant (Guangzhou, China).

Synthesis of a monomeric quaternary salt based on N,N-dimethylamino-ethyl methacrylate with ethyl iodide (DMAEMA · IE). We poured 1 mol (156 g) of ethyl iodide and 133 ml of absolute acetone as a solvent and 1 mol (157 g) of N,N-dimethylaminoethyl methacrylate into a conical flask. Then the solution was subjected to periodic stirring on a magnetic stirrer at a temperature of 298-293K. After 10-15 minutes, white crystals begin to precipitate.

The duration of the reaction is 5-6 hours. Resulting white crystals were washed with ether

and dried in a vacuum desiccator at room temperature. The obtained monomer salt was recrystallized twice with an acetone-alcohol solution at a ratio of 9:1. The salt yield is 95-98%. $T_m = 375K$.

The synthesis of the DMAEMA · IPI monomer salt was carried out according to the above described procedure. To obtain polymers by the gravimetric method, ampoules made of molybdenum glass were washed with a chromium mixture and distilled water, then 1-5 cm³ of a mixture of monomers containing a certain amount of initiator was poured into the ampoules. The ampoules with the contents were connected to a vacuum dosing unit and degassed to a residual pressure of 10⁻³ mm Hg. by triple freezing with liquid nitrogen, pumping out the system in this state and further defrosting.

The ampoules were sealed and placed in a thermostat with the required temperature, where polymerization was carried out depending on the temperature and duration of the reaction. After the time elapsed, the ampoules were opened, the resulting polymers were isolated by precipitation into acetone and purified by double reprecipitation and from dimethyl sulfoxide into acetone. Then the polymer was dried to constant weight in vacuum at room temperature and the yield was determined.

The kinetics of polymerization was studied by the dilatometric method [15], which is based on the change in the volume of the reaction mixture as a result of the conversion of monomers into a polymer. The degree of conversion of the monomer into polymer was determined by the formula:

$$q = \Delta V / V \cdot K \cdot 100\%$$

where:

ΔV - change in the volume of the reaction mixture for a given period of time;

V - is the initial volume of the monomer at the reaction temperature;

K - is the contraction coefficient, which determines the changes in the volume of the monomer mixture at a given temperature as a result of the complete conversion of the monomer into polymer.

The density of the monomer and polymer was calculated using the known formula [15]. The viscosity of dilute polymer solutions was measured in capillary viscometers of the Ubbelohde type. Intrinsic viscosity was determined by double graphical extrapolation of reduced viscosity and η_{OTH}/C to zero concentration [15].

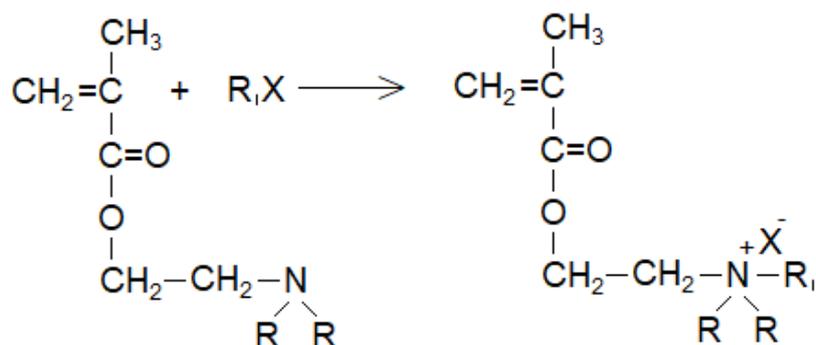
IR spectra were recorded on a Spekord UR-20 spectrometer. Samples were prepared by pressing into tablets with potassium bromide.

NMR spectra were recorded on a Varian T-60 spectrometer with an operating frequency of H-60 MHz nuclei at room temperature. Deuterated trichloromethane and dimethylsulfoxide were used as a solvent, and tetramethylsilane was used as an internal standard.

Electronic absorption spectra were recorded on a Hitachi-330 spectrophotometer using quartz cuvettes 0.5 cm thick in the wavelength range 200-450 nm.

Results and discussion

Monomeric quaternary salts based on N, N-dimethylaminoethyl methacrylate with ethyl iodide (DMAEMA·IE) and isopropyl iodide (DMAEMA·IPI) have been synthesized, and their radical polymerization at low temperatures (293-313K) was studied. Quaternization reactions of DMAEMA·IE, DMAEMA·IPI can be described by the following scheme:



where R - CH₃; R₁-CH₂-CH₃;CH₃-CH-CH₃.

The obtained soybeans are dissolved in water, ethyl alcohol, dimethylformamide, dimethyl sulfoxide, acetonitrile. The synthesized monomeric salts were identified using IR and PMR spectra and the results of elemental analysis (Table 1, 2).

Table 1 Elemental composition of monomeric quaternary salts

Name monomers	Calculated,%				Found,%			
	C	H	N	J	C	H	N	J
DMAEMA·IE	38,3	6,4	4,5	40,6	38,6	6,3	4,6	40,7
DMAEMA·IPI	40,4	6,7	4,2	38,8	40,1	6,9	4,3	38,9

Table 2

	DMAEMA·IE	DMAEMA·IPI
IR spectra	1634 cm ⁻¹ (C=C groups), 3900 cm ⁻¹ (⁺ NH ₄); 1720 cm ⁻¹ (C = O stretching vibration); 1180 cm ⁻¹ (asymmetric stretching vibration C-O-C); 1460, 1300, 980 cm ⁻¹ (CH ₂ , CH ₃ , C-CH ₂ stretching vibration).	1640cm ⁻¹ (C=C groups), 3950cm ⁻¹ (⁺ NH ₄); 1730 cm ⁻¹ (C = O stretching vibration); 1100 cm ⁻¹ (asymmetric stretching vibration C-O-C); 1480, 1280, 980 cm ⁻¹ (CH ₂ , CH ₃ -CH-CH ₃ , C-CH ₂ stretching vibration).
¹H- nuclear magnetic resonance	a (5.70 ppm), b (6.20 ppm), c (1.50 ppm), d (4.70 ppm), e (3.70 ppm - one), f (3.20 ppm), g (3.50 ppm).	a (5.73 ppm), b (6.10 ppm), c (1.25 ppm), d (4.60 ppm), e (3.60 ppm - one), f (3.20 ppm), g (3.80 ppm).

Preliminary experiments have established that the monomers DMAEMA·IE, DMAEMA·IPI practically do not polymerize in the absence of radical initiators. However, their polymerization is carried out easily with the addition of a radical initiator at a temperature of 293-313K in organic solvents. Studies of the influence of the nature of solvents on the process of polymerization of the nature of solvents showed that with an increase in the dielectric constant of the solvent in the series ethanol, dimethylformamide, dimethyl sulfoxide, water, the rate of polymerization and the intrinsic viscosity of the resulting polymers increase (Table 3).

Table 3. Influence of the nature of solvents on the polymerization of monomeric quaternary salts. T = 293K; [M] = 1.1 mol; [DAK] = 4·10⁻² mol / l.

Monomer salt type	Solvent	Speed reaction, V _p ·10 ⁻⁶ , mol/l·s	[η], dl/g in 0.1N KCl
DMAEMA·IE,	Этанол	0,26	1,8
	ДМФА	0,53	4,5
	ДМСО	0,96	6,2
DMAEMA·IPI	Этанол	0,10	1,5
	ДМФА	0,24	3,2
	ДМСО	0,75	5,1

This could be due to an increase in the dielectric constant of solvents or an increase in the rate constant of chain growth in polar and protic solvents. The polymerization of these monomers in water solutions was not carried out in the same way as a non-water-soluble AIBN initiator was used under the reaction conditions at 293–313 K.

The influence of the monomer and initiator on the polymerization process was studied in a wide range of their concentrations up to low conversions - 10-12%. With an increase in the concentration of monomeric salts and initiator, the rate of the polymerization reaction naturally increases. The logarithmic dependence of the rate of polymerization of the monomer and initiator is linear. The reaction orders for the monomers DMAEMA·IE, DMAEMA·IPI are 1.4 and 1.5, respectively, for the initiator concentration of 0.5, which indicates the bimolecular nature of chain termination.

Based on the results of kinetic studies, the total rate of polymerization of monomeric quaternary salts in the presence of an initiator at moderate temperatures is described by the equation:

$$V = K [M]^{1.4} [I]^{0.5}$$

$$V = K [M]^{1.5} [I]^{0.5}$$

To clarify the dependence of the yield and polymerization rate on temperature, the reaction was carried out in the temperature range 303-318K. From the temperature dependence of the constants of the initial reaction rate, the total activation energies of polymerization of DMAEMA·IE, DMAEMA·IPI were determined, which turned out to be equal to 53.7 kJ / mol and 41.8 kJ / mol, respectively.

It was found that the studied polymerization is completely inhibited by effective inhibitors of radical polymerization, such as 2,2,6,6-tetramethylpiperidyl-1-oxyl (TMPO), hydroquinone, and air oxygen. These data, as well as the EPR "spin trap" method, assert that the polymerization of the indicated monomeric salts in the absence of thermal decomposition of the initiator is of a radical nature. By inhibiting the polymerization reaction in the presence of TMPO, the rate of the initiation reaction in the DMAEMA·IPI-initiator systems was determined (table 4).

Table 4 Kinetic parameters of polymerization of DMAEMA · IPI in the presence of the inhibitor TMPO, T = 313K. Initiator - DAK.

Concentration		$V_p \cdot 10^{-6}$, mol/l·s	$V_{in} \cdot 10^{-9}$, mol/l·s	$K_p/K_o^{0.5}$
monomer, mol/l	initiator, 10^{-2} , mol/l			
1,0	1,0	3,15	0,11	3,18
1,0	2,0	4,52	0,12	4,04
1,0	3,0	5,25	0,16	3,94
1,5	2,0	6,0	0,20	4,48

Thus, the occurrence of the polymerization reaction at temperatures excluding the thermal decomposition of the initiator AIBN, the overestimated value of the reaction order with respect to the monomer, and the available literature sources suggest that polymerization under these conditions proceeds due to the donor-acceptor interaction [16-18].

As a result of the reaction of the donor-acceptor interaction of the indicated monomeric salts with the initiator AIBN, a complex compound "monomer-initiator" is formed, capable of decomposing into free radicals, initiating the polymerization process at low temperatures. An

external manifestation of the formation of a complex compound is that when mixing solutions of iodine-containing monomers and an initiator, the mixture becomes pale yellow. This indicates the formation of a new compound of the charge transfer complex.

To obtain reliable information on the process of complexation of the monomer salt with the initiator, electron spectroscopy studies were carried out in the wavelength range of 260-500 nm (Fig. 1).

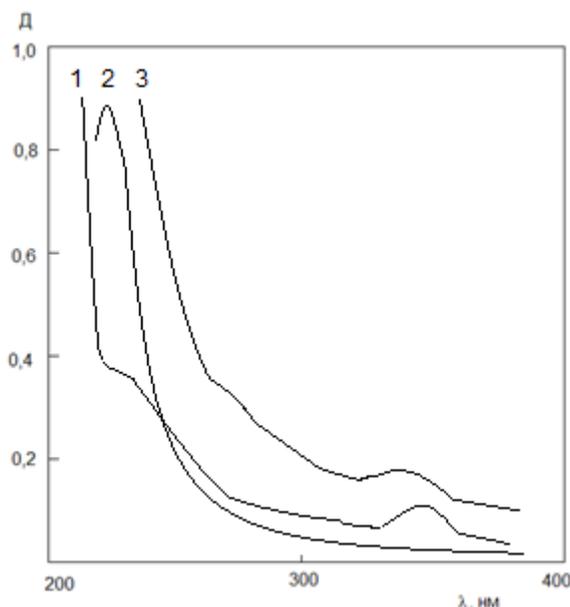


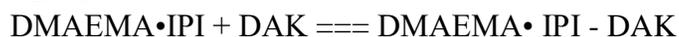
Figure 1. Electronic absorption spectra: 1-DAA, 2-DMAEMA·IPI, 3- combined solutions $[DMAEMA \cdot IPI] + [DAA] = 4 \cdot 10^{-4} \text{ mol}^{-1}$; $T=298\text{K}$.

In the electronic spectra of the combined solutions of DMAEMA·IPI and AIBN, new absorption bands appear, shifted to longer wavelengths at 346 nm, which is absent in the spectra of the initial components. The formation of a new band indicates the existence of a donor-acceptor molecular complex characterizing the transfer of an electron from one molecule to another.

The composition of the resulting complex was determined by the "isomolar series" method. The dependence of the optical density of the DMAEMA·IPI-DAK system on the component ratio passes through a maximum, and the maximum optical density corresponds to the equimolar composition of the components, and the following equilibrium exists in the solution of this system:



whena = b = 1



then the equilibrium constant of this reaction is

$$K_s = C_{DMAEMA \cdot IPI-DAK} / C_{DMAEMA \cdot IPI} \cdot C_{DAK}(2)$$

Where: $C_{DMAEMA \cdot IPI}$, C_{DAK} , $C_{DMAEMA \cdot IPI-DAK}$ - equilibrium concentrations of DMAEMA·IPI, DAK and equimolar complex.

Taking into account the dependence of optical density on concentration, the following equation can be written:

$$K_c = D_k \varepsilon_k / C_{DMAEMA \cdot IPI} \cdot \varepsilon_k - D_k (C_{DAK} \varepsilon_k - D_k) \quad (3)$$

where: D_k is the optical density of the complex, ε_k is the molar extinction coefficient of

the complex, l is the width of the cell, $C_{\text{DMAEMA}\cdot\text{IPI}_0}$, C_{DAK_0} are the initial concentrations of the monomer salt and initiator.

Equation (3) was transformed into:

$$C_{\text{DMAEMA}\cdot\text{IPI}}^0 C_{\text{DAK}}^0 l / D_k (C_{\text{DMAEMA}\cdot\text{IPI}}^0 + C_{\text{DAK}}^0) = 1 / K_c \epsilon_k (C_{\text{DMAEMA}\cdot\text{IPI}}^0 + C_{\text{DAK}}^0) + 1 / \epsilon_k \quad (4)$$

Measurements of the optical density at a constant concentration of one of the reagents of the system with a change in the concentration of the other in time show that their spectra have one maximum. The data suggest that a complex of the same type is formed in the DMAEMA • IPI – DAK system. The values of the complexation constant (K_c) and the coefficient of molar extinction of the complex (ϵ_k) were found graphically for the DMAEMA•IPI - DAK system, equal to: $K_c=41.7 \text{ liters}\cdot\text{mol}^{-1}$, $\epsilon_k = 11.3 \text{ l}\cdot\text{mol}^{-1} \text{ cm}^{-1}$.

The calculated thermodynamic parameters of the molecular complex — enthalpy of formation of the complex (ΔH), free energy of formation of the complex (ΔG), entropy (ΔS) have the following values: $\Delta H = -39.6 \text{ kJ / mol}$; $\Delta G = -13.5 \text{ kJ / mol}$; $\Delta S = -0.089 \text{ kJ / mol deg}$. The data obtained show that as a result of the binding of DMAEMA • IPI and AIBN into molecular complexes, the number of degrees of freedom of motion of the molecules of the system decreases, that is, the entropy decreases. The H value indicates the relatively weak character of the complex compound.

Conclusion

1. The possibility of carrying out controlled complex-radical polymerization of

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