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Synthesis and Characterization of N,N-Dimethylacrylamide and [(3-Methacryloyl-amino)propyl]trimethylammonium Chloride Copolymers: Kinetics, Reactivity, and Biocidal Properties

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Abstract

In this work, a copolymer of N,N-dimethylacrylamide (DMAA) and [(3-methacryloyl-amino)propyl]trimethylammonium chloride (TMAPMACh) with different molar compositions was synthesized by the free radical copolymerization in an aqueous medium in the presence of ammonium persulfate ($(NH_4)_2S_2O_8$) as an initiator. The functional and molar composition of the synthesized copolymers was determined by conductometric titration, Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. Reactivity coefficients of the monomers were determined using Mayo-Lewis ($r_{TMAPMACh} = 1.25 \pm 0.02$ and $r_{DMAA} = 2.00 \pm 0.02$) and Fineman-Ross ($r_{TMAPMACh} = 1.16 \pm 0.02$ and $r_{DMAA} = 2.25 \pm 0.02$) methods. The influence of the concentration of monomers [M] and initiator [I] on the rate of copolymerization reaction (R_C) at 333 K and equimolar ratios of monomers in the initial mixture was investigated. The kinetic equation of the copolymerization reaction of DMAA with TMAPMACh was derived: $R_C = k \times [M]^{2.70} \times [I]^{1.24}$. The average rate constant of the copolymerization reaction at this temperature was equal to $k = 9.72\ L^{2.94} \times mol^{-2.94} \times s^{-1}$. It was also found that the copolymers DMAA-TMAPMACh have a biocidal effect against thionic bacteria *Thiobacillus ferrooxidans* (TB) at a minimum concentration of 1.0 wt. %. Although they do not exhibit bactericidal effects against sulfate-reducing bacteria (SRB) bacteria, they do delay their growth at a concentration of 0.2/1.0 wt. %.

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1. Introduction

Metal corrosion, including on metal products and structures, is one of the biggest challenges facing industries today.[1-8] Corrosion leads to significant financial losses for countries` economies. Every year, over 20% of metal structures fail as a result of corrosion. Annual economic losses caused by corrosion amount to 3/3.5% of the gross national product of developed countries. The contribution of microbiological corrosion to the total amount of damage is 20/40%.[9,10]

Microbiological corrosion (biocorrosion) is the destruction of materials (especially constructions) in the presence of various microorganisms living in air, water and soil. Usually, microorganisms are not corrosively aggressive. But the substances released during the metabolism (life activity) of microorganisms are corrosively aggressive.[1,11,12]

Biological corrosion is classified into two categories based on the microorganism type: mycological and bacterial. Of the two, bacterial corrosion is the most prevalent in nature.[13-15] Mycological corrosion is the destruction of metals and metal coatings under the influence of aggressive substances formed during the activity of mycelial fungi.

Bacterial corrosion occurs in the presence of bacteria at pH 1.0/10.5, and in most cases at 6-45 °C, in the presence of organic and inorganic compounds containing oxygen, carbon,

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hydrogen, iron, nitrogen, potassium, sulfur and other elements. Among bacteria sulfate-reducing Desulfovibrio and Desulfotomaculum species, sulfate-reducing bacteria (SRB) and thion (Tiobacilus species, TB) bacteria are considered the most dangerous.[16]

SRB live in anaerobic (oxygen-free) conditions at 25/44 ℃ and pH 5.5/9.0.[16,17] SRB creates energy reserves by reducing sulfates, sulfites, thiosulfates, and tetrathionates. They use organic compounds as electron donors.[18-21] Although SRB are anaerobic bacteria, they are resistant to the effects of air and stable up to 80 ℃. Therefore, they are often found in soil, fresh and sea water, and in geological deposits of sulfur and oil.

SRB convert sulfates and sulfites into hydrogen sulfide.[22] Under the influence of hydrogen sulfide, metals are converted into sulfides and hydroxides, *i.e.* metal structures are destroyed.[23-25]

Thionic bacteria (TB) are microorganisms that convert sulfur compounds into sulfates and sulfuric acid.[26-29] TB have enzymatic properties. They are aerobic bacteria.

In most cases, during the metabolism of microorganisms, acid is released into the medium, and as a result, the pH of the medium changes.[30-32] Moisture and the presence of organic and inorganic substances, oil, and salt solutions in the environment also accelerate the biological corrosion of concrete and reinforced concrete installations.

Biocides are employed to safeguard metals and non-metallic materials from biocorrosion and used against harmful microorganisms. Biocides include pesticides, fungicides, herbicides, insecticides, antiseptics and antibiotics. A range of chemical compounds can act as biocides (alcohols, phenols and their derivatives; aldehydes, ketones, organic acids and their derivatives; amines and amine salts, quaternary ammonium compounds; organoelement compounds, *etc*.) The choice of biocide depends on the composition of the protected material and the specific microorganism responsible for the corrosion.

In most cases, in order to protect metal equipment and building materials from biological corrosion, their surface is treated with bactericides, or fungicides (protection against fungi) and bactericides that are added to the lacquering materials applied to their surface.[33-35]

The results of many studies have shown that the treatment of material surfaces with low molecular weight biocides is ineffective. The main reason is that such protective layers are brittle, have poor adhesion to the surface, and are quickly washed away by water.[36]

Although many types of biocides have been synthesized[34-36], it is difficult to say that currently used biocidal compounds are able to completely protect materials from biocorrosion. One of the reasons is that microorganisms are able to quickly adapt to various materials, environmental changes and the action of biocidal compounds.[33-38] Frequent suppression of the growth of microorganisms by the same compound can create conditions for the development of mutants resistant to the action of the biocide.[33,37] For this reason, mixtures of biocides are often used to prevent the development of mutant strains.

Among biocides, polymer-based biocidal coatings offer reliable and long-term protection against biocorrosion.[39-44] Biocidal polymer compounds are typically categorized into the following groups:[45]

- polymers containing biocidal organic compounds;
- polymers containing biocidal inorganic additives;
- polymers that acquire biocidal properties through chemical modification;
- polymers with their own biocidal activity;
- polymer nanocomposites.

Among these compounds, polymers with their own biocidal properties are of great interest, because there is no need to introduce additional biocidal compounds into the polymers' composition.

Nowadays, many biocidal polymers based on esters and amide derivatives of (meth)acrylic acids are known.[39,46-50] Among polymeric biocides, cationic biocides are considered to have a great future. This is because according to the accepted view[18,27] the cationic polyelectrolyte dissolved in water can interact with the "negatively" charged microorganisms` surface through an electrostatic mechanism, and as a result forming a thin adsorption layer on the cell surface. This adsorption layer blocks the movement of oxygen and nutrients to the microorganism's cells, leading to its death. According to the second viewpoint, the biocide molecules penetrate the cell, inhibit enzymes of the respiratory chain and disrupt phosphorylation processes through oxidation. This interaction with the biocide can even lead to the misfolding of cytoplasmic proteins.[42,51,52]

Authors of[53-55] obtained microspheres from a mixture of poly(4-vinylpyridine) and polyvinylidenefluoride. Then by quaternization of pyridine groups with alkyl bromide, cationic microparticles with antibacterial properties were synthesized that can be used against fungi.

In [56] a method of increasing the antimicrobial activity of the silicone surface by covalently planting [3-(methoxysilyl)propyl]dimethyloctadecylammonium chloride on the rubber surface was developed. It was observed that following surface treatment, the bacteria's adherence to the rubber surface significantly decreased.

In [57] by copolymerization of [3-(methylacryloylamino)

propyl]trimethylammonium chloride with [3-trimethylsilyl) propyl]methacrylate a polymeric compound with antimicrobial properties was synthesized. It was proven the toxicity of the synthesized polymeric compound to human cells was significantly lower compared to that of existing molecular antimicrobial agents.

Currently, copolymers based on N,N-dimethyl-N,N-diallylammonium chloride (DMDAACh) can be considered as widespread cationic polymers. These include cationic copolymers of DMDAACh with acrylamide (AA),[58] N,N-dimethylacrylamide (DMAA),[59-62] 2-(diallyl(methyl)ammonio)acetate (DAMAA),[63] acrylonitrile (AN), (meth)acryloylethyl trimethylammonium chloride (M)AETEACh), dimethylaminoethyl methacrylate (DMAEMA),[63] maleic acid (MA),[64] vinyl ether of monoethanolamine (VEMEA)[65,66] among others [67-73]. Polymers containing a quaternary ammonium group have a biologically active properties of low molecular quaternary ammonium compounds and physicochemical properties of high molecular (polymeric) compounds.[36] Therefore, most of such polymeric compounds have also biocidal (bactericidal) properties. However, most of cationic polymers are not widely used in practice. The main reasons are the high cost of monomers required for synthesis, the slow rate of copolymerization reactions or the low reaction yield. All of this ultimately increases the cost of the copolymer.

Therefore, developing new, effective polymeric biocidal compounds using readily available industrial monomers and expanding the range of these types is an urgent task.

The purpose of this work is to synthesize a new polymeric biocidal compound and explore its properties. For this purpose, N,N-dimethylacrylamide (DMAA) and [(3-methacryloylamino)-propyl]trimethylammonium chloride (TMAPMACh) were selected as monomers.

2. Experimental

2.1 Materials

N,N-dimethylacrylamide (DMAA) (purity 99.9 %) and acetone (purity 99.9 %) were purchased from Sigma Aldrich Ltd.

[(3-methacryloylamino)propyl]trimethylammonium chloride (TMAPMACh) was used as a 95 wt. % solution in water. (Sigma Aldrich Ltd.)

Ammonium persulfate ($(NH_4)_2S_2O_8$) (APS, purity 99.7 wt. %) was kindly provided by LaborPharma Ltd. (Almaty, Kazakhstan). Argon gas (purity 99.995 wt. %) was kindly provided by IkhsanTechGas (Almaty, Kazakhstan). Distilled water with a conductivity 2.4 μS/cm at 20 °C was used in all experiments.

2.2 Methods

The functional and molar compositions of the copolymers were determined by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy and conductometric titration of the chloride anions of the copolymer with an $AgNO_3$ solution.

The IR spectrum of the DMAA-TMAPMACh copolymer sample was recorded on a Nicolet 5700 spectrometer, Termo Corporation, USA in the frequency range of 4000-500 cm^{-1}. To do this, 1.5 mg of the copolymer was mixed with 200 mg of KBr salt, and then the mixture was compacted to obtain a tablet. This tablet was then used to take the IR spectrum.

^1H NMR spectra were recorded on a JNM-ECA Jeol 400 spectrometer (frequency 399.78 MHz) using D_2O as the solvent at 20 °C. The NMR spectrum of the copolymer synthesized from the mixture [DMAA]:[TMAPMACh]=50:50 mol.% was recorded. Chemical shifts were measured relative to the residual proton signals of the deuterated solvent.

Conductometric titration was carried out using a TDC/Salinitymeter 902 conductometer.

The pH of the copolymer solution was determined using a pH meter.

The copolymer yield (y, wt. %) was determined by the gravimetric method using the following equation:

$$y = m_{cop} \times 100\%/m_{mon}, \quad (1)$$

where, m_{cop} is the mass of copolymer; m_{mon} is the total mass of monomers in the initial monomers' mixture.

The biocidal properties of the DMAA-TMAPMACh copolymer with different molar compositions against the growth of sulfate-reducing bacteria (SRB) and thionic bacteria Thiobacillus ferrooxidans (TB) were studied in the Laboratory of Environmental and Agricultural Microbiology of the Research and Production Center for Microbiology and Virology, Ltd. (Almaty).

2.3 Methodology for determining the order of a copolymerization reaction by monomer and initiator

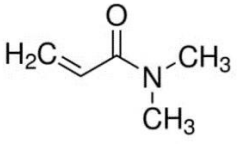
To determine the reaction order by monomer, copolymerization was carried out in a constant volume of solution, a constant concentration of the initiator in the solution, a constant molar ratio of monomers (for example, 50:50 mol. %) and a different total concentration of monomers.[74] At a selected temperature, for each total monomer concentration, copolymerization is carried out and the copolymer yield is determined at certain time intervals. Then, based on the obtained data, a graph of the dependence of the copolymer yield on the duration of the copolymerization reaction was created. The rate of the copolymerization

reaction for each concentration was determined (R_c(mol/(L×min)) from the slope of the initial portion of the curves "the yield versus time" (y = f(t)). Subsequently, a graph of log R_c versus log [M] is plotted ([M] is the concentration of the monomer, mol/L). The slope of the resulting straight line (tgα) was equal to the order of the copolymerization reaction by monomer.[74]

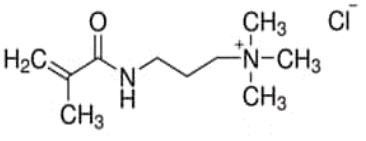
To determine the reaction order by initiator, copolymerization was performed in a constant volume of solution, a constant concentration of the monomers in the solution, a constant molar ratio of monomers (for example, 50:50 mol. %) and varying concentrations of initiators.[74] At a selected temperature, for each initiator concentration, copolymerization was performed and the copolymer yield was determined at certain time intervals. Then, based on the obtained data, a graph of the dependence of the copolymer yield on the duration of the copolymerization reaction was created. The rate of the copolymerization reaction for each initiator concentration was determined (R_c(mol/(L×min)) from the slope of the initial portion of the curves "the yield versus time" (y = f(t)). Subsequently, a graph of log R_c versus log [I] was plotted ([I] is the concentration of the initiator, mol/L). The slope of the resulting straight line (tgα) was equal to the order of the copolymerization reaction by initiator.[74]

2.4 Synthesis of copolymers

For the synthesis of the cationic copolymer, the monomers N,N-dimethylacrylamide (DMAA) and [3-(methacryloylamino)propyl]trimethylammonium chloride (TMAPMACh) were chosen (Fig. 1):



DMAA



TMAPMACh

Fig. 1 Structural formulas of the DMAA and TMAPMACh monomers.

The main reasons for choosing these monomers are:

1) both monomers are produced on an industrial scale, i.e. available and relatively cheap;

2) both monomers have a positive charge so the synthesized copolymer will exhibit the properties of a cationic polyelectrolyte. In addition, both monomers demonstrate bactericidal properties, so the DMAA-TMAPMACh copolymer (Fig. 2) can be used as a biocidal polymer to suppress the growth of microorganisms and bacteria that cause microbiological corrosion of metals and metal structures.

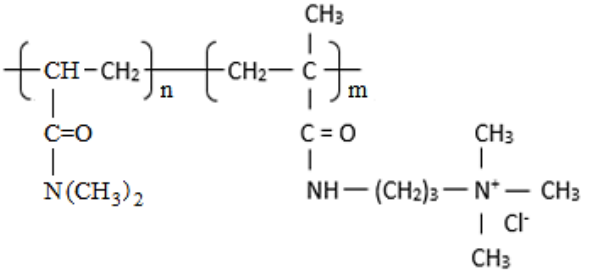


Fig. 2 Structural formula of the DMAA-TMAPMACh copolymer.

The copolymer DMAA-TMAPMACh with the structural formula was synthesized in ampoules by free radical copolymerization of monomers in an aqueous medium. To do this, the calculated amounts of monomers and initiator were placed in an ampoule, then the total volume of the mixture was brought to the required value by adding distilled water. After this, in order to remove oxygen, the mixture was purged with an inert (argon) gas for 15 minutes and then the ampoule was immediately sealed. Further the ampoule with the reaction mixture was placed in a thermostat and heated at a temperature of 333 K for 3 hours.[60,61]

Ammonium persulfate (APS), $(NH_4)_2S_2O_8$, was used as an initiator. The concentration of the initiator varied between 0.05/0.2 wt. % and the total concentration of monomers varied between 0.5-2 mol/L.

The synthesized copolymers were separated from the reaction medium by precipitation and washing several times with acetone. After this, the copolymers were dried at a temperature of 313 K under vacuum for several days until the mass of the samples stabilized. The DMAA-TMAPMACh copolymers are gray amorphous substances that are highly soluble in water.

3. Results and discussion

3.1 Determination of the molar composition of the synthesized copolymers

In this work, the effect of molar concentrations of monomers in the initial reaction mixture on the copolymer composition and yield was studied. The molar composition of synthesized copolymers was determined by the method of conductometric titration of chloride anions of the TMAPMACh monomer with $AgNO_3$ solution. The obtained experimental values are presented in Table 1.

Table 1. Results of determination of DMAA-TMAPMACh copolymer composition by conductometric titration.

№	The mole fraction of monomers in the initial mixture, mol. %		The mole fraction of monomers in the copolymer, mol. %		Concentration of the monomers in the mixture, mol/L	Copolymer yield
	M_1 (TMAPMACh)	M_2 (DMAA)	m_1 (TMAPMACh)	wt %		
1	80	20	78	22		43.2
2	60	40	56	44		53.4
3	50	50	41	59		57.1
4	40	60	28	72	1.0	58.9
5	20	80	10	90		62.7

Based on the data in the table, we can do the following conclusion: in the radical copolymerization reaction, DMAA is more active than the second monomer (TMAPMACh). Therefore, the amount of DMAA in copolymers is always higher than its molar amount in the initial mixture. Furthermore, with an increase in the mole fraction of the DMAA monomer in the initial mixture, the yield of the copolymer rises.

To determine the functional and molar composition of the synthesized DMAA-TMAPMACh copolymer, IR and ^{1}H NMR spectra were recorded.

3.2 Analysis of the IR spectrum of the DMAA-TMAPMACh copolymer

Figure 3 shows the IR spectrum of the DMAA-TMAPMACh copolymer synthesized from a mixture of monomers with a molar composition of 50:50 mol. %. In the spectrum, a peak corresponding to the carboxyl C=O group is visible at 1622 cm^{-1}. The peak at the frequency of 3363 cm^{-1} corresponds to the secondary amide group and the peaks at the frequency of 2358 and 2339 cm^{-1} correspond to the methyl -CH_3 and methylene groups -CH_2- respectively. Signals of C-N and C-NH deformation vibrations of the copolymer groups appear at 1525 cm^{-1} and 1477 cm^{-1}.[75,76] Therefore, based on the IR spectrum, we can say that DMAA and TMAPMACh monomers are included in the copolymer composition.

3.3 Analysis of the ^{1}H NMR spectrum of the DMAA-TMAPMACh copolymer in D_2O

Figure 4 shows the ^{1}H NMR spectrum of the DMAA-TMAPMACh copolymer synthesized from the mixture [DMAA]:[TMAPMACh]=50:50 mol. %. Chemical shifts are measured relative to the residual proton signals of the deuterated solvent.

The ^{1}H NMR spectrum of the DMAA-TMAPMACh copolymer is characterized by the presence of signals centered at 0.85; 1.90; 2.79; 3.04 and 3.25 ppm. The attribution of each NMR signal to the protons of a particular fragment of the DMAA-TMAPMACh copolymer and the integral proton intensity are presented in the figure. Determination of the molar ratio of TMAPMACh fragments to DMAA based on the integral intensities of the methylene protons of TMAPMACh and the methine protons of DMAA and the total ratio of proton integral ratios of the studied fragments showed that in the copolymer there are 1.56 base-moles of DMAA per 1 base-mole of TMAPMACh. This value is very close to the composition (1.44:1) determined by conductometric titration (Table 1).

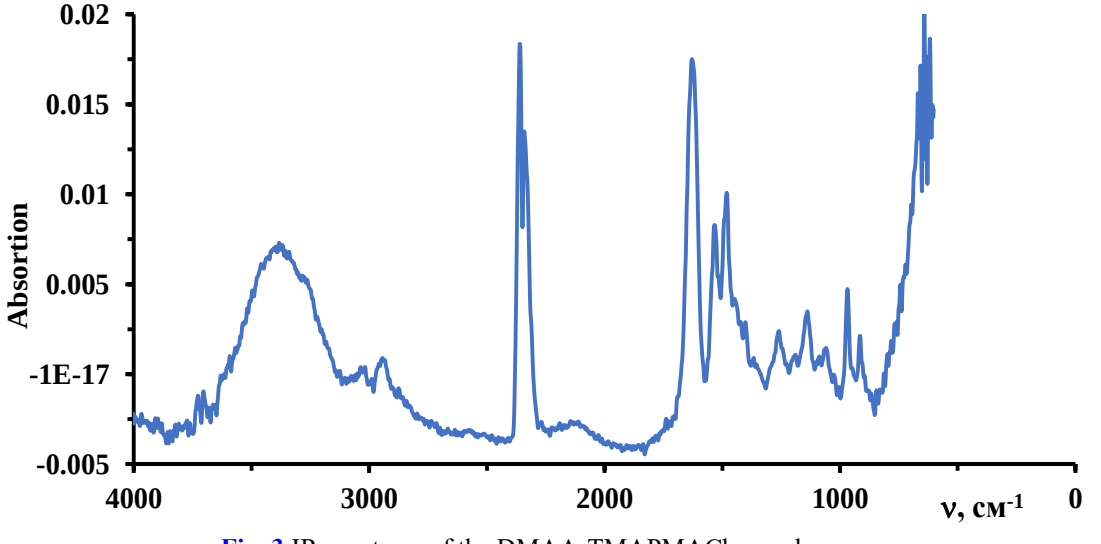


Fig. 3 IR spectrum of the DMAA-TMAPMACh copolymer.

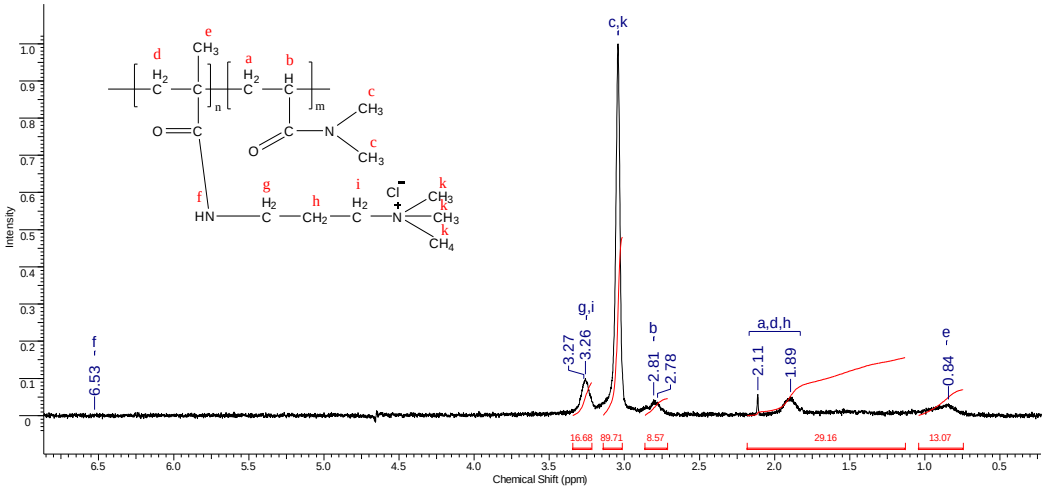


Fig. 4 ^{1}H NMR spectra of the DMAA-TMAPMACh copolymer in D_2O.

3.4 Calculation of the reactivity of monomers

A quantitative characteristic of the reactivity of monomers is the copolymerization constants or their reactivity coefficients. The reactivity coefficients of the monomers in the radical copolymerization reaction were calculated by the Mayo-Lewis (2) and Fineman-Ross (3) equations using the data in Table 1.[77,78]

$$r_2 = F\times\{(1/f)\times(F\times r_1 + 1) - 1\}; \quad (2)$$

$$(F/f)\times(f\text{-}1) = r_1\times(F^2/f) - r_2 \text{ or } y = r_1\times x - r_2; \quad (3)$$

$$F = [M_1] / [M_2]; \quad f = [m_1] / [m_2], \quad (4)$$

where, $[M_1]$ and $[M_2]$ are the mole fractions of monomers in the initial mixture, %; $[m_1]$ and $[m_2]$ are the mole fractions of monomers in the copolymer, %; $x = (F^2/f)$; $y = (F/f) \times (f-1)$.

The reactivity coefficients of the monomers represent the ratio of the rate constants of addition of "native" and "alien" monomers to a given active center: $r_1 = k_{11} / k_{12}$ and $r_2 = k_{22} / k_{21}$. Thus, they characterize the selectivity of chain growth reactions.

The value $(1/r_1) = (k_{12}/k_{11})$ is the ratio of the rate constant for the reaction of adding monomer 2 to monomer 1 to the rate constant for the homopolymerization reaction of monomer 1. Then, the value $(1/r_2) = (k_{21}/k_{22})$ is equal to the ratio of the rate constant for the reaction of adding monomer 1 to monomer 2 to the rate constant for the homopolymerization reaction of monomer 2.[78]

The calculation results are listed in Tables 2 and 3, and graphs based on the tabulated values are shown in Fig. 5.

Table 2. Calculation of the reactivity coefficients of monomers by the Mayo-Lewis method.

The mole fraction of monomers in the initial mixture, mol. %		The mole fraction of monomers in the copolymer, mol. %		Copolymer yield, wt %	$F = [M_1] / [M_2]$	$f = [m_1] / [m_2]$	$r_2 = F\times\{(1/f) \times (F\times r_1 + 1) - 1\}$	r_1	r_2
M_1 (TMAPMACh)	M_2 (DMAA)	m_1 (TMAPMACh)	m_2 (DMAA)						
80	20	78	22	43.2	4.00	3.50	$r_2 = 4.57\times r_1 - 2.86$		
60	40	56	44	53.4	1.50	1.27	$r_2 = 1.77\times r_1 - 0.32$		
50	50	41	59	57.1	1.00	0.69	$r_2 = 1.45\times r_1 + 0.45$	1.25	2.00
40	60	28	72	58.9	0.67	0.39	$r_2 = 1.15\times r_1 + 1.05$		
20	80	10	90	62.7	0.25	0.11	$r_2 = 0.57\times r_1 + 2.02$		

Table 3. Calculation of the reactivity coefficients of monomers by the Fineman-Ross method.

The mole fraction of monomers in the initial mixture, mol. %		The mole fraction of monomers in copolymer, mol. %		Copolymer yield, wt %	$F = [M_1] / [M_2]$	$f = [m_1] / [m_2]$	$x = (F^2/f)$	$y = (F/f)\times(f\text{-}1)$	r_1	r_2
M_1 (TMAPMACh)	M_2 (DMAA)	m_1 (TMAPMACh)	m_2 (DMAA)							
80	20	78	22	43.2	4.00	3.50	4.57	2.86		
60	40	56	44	53.4	1.50	1.27	1.77	0.32		
50	50	41	59	57.1	1.00	0.69	1.44	-0.44	1.16	2.25
40	60	28	72	58.9	0.67	0.39	1.14	-1.05		
20	80	10	90	62.7	0.25	0.11	0.56	-2.00		

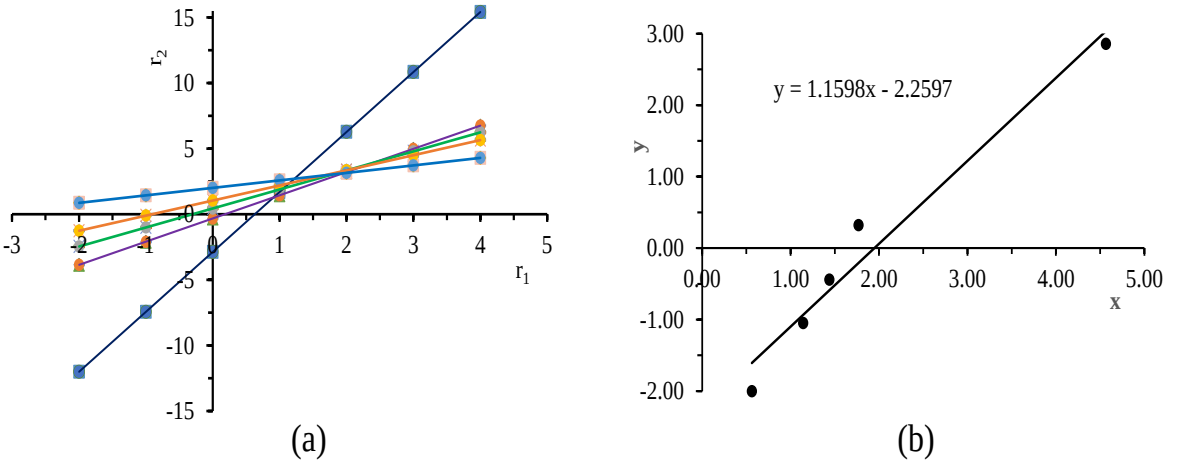


Fig. 5 Calculation of the reactivity coefficients of monomers in the DMAA-TMAPMACh system from graphs using the Mayo-Lewis (a) and Fineman-Ross (b) methods.

The reactivity coefficients of the monomers TMAPMACh (1) and DMAA (2), calculated by various methods, are given in Table 4. The copolymerization constants calculated by different methods are close in value, and their multiplication is greater than one. It indicates a chaotic distribution of monomers in the copolymer chain.[78-80]

Table 4. Comparison of the reactivity coefficients of the monomers TMAPMACh (1) and DMAA (2), calculated by different methods.

Method	r_1	r_2	$1/r_1$	$1/r_2$	$r_1 \times r_2$
Mayo-Lewis	1.25	2.00	0.80	0.5	2.25
Fineman-Ross	1.16	2.25	0.86	0.4	2.61

Comparing the tabular data, we can draw the following conclusion: in the radical copolymerization reaction, the DMAA monomer is significantly more active than the TMAPMACh monomer. As a result, the mole fraction of DMAA in the DMAA-TMAPMACh copolymer is always greater than its amount in the original mixture. Additionally, it should be noted that during the radical copolymerization reaction, DMAA-TMAPMACh copolymers with random composition are formed.[60,74,80]

The relatively lower activity of the DMAPMACh monomer in the radical copolymerization reaction can be explained by the presence of a positive charge in the composition and the complex spatial structure (steric effect) of this monomer.[61,62] The attachment of a charged monomer to a macrochain ending with DMAPMACh is extremely difficult due to the repulsion of similarly charged particles.

3.5 Effect of concentration on the copolymer yield

In this study the effect of the concentration of initiator ($(NH_4)_2S_2O_8$) on the copolymer yield was also examined (Fig. 6).

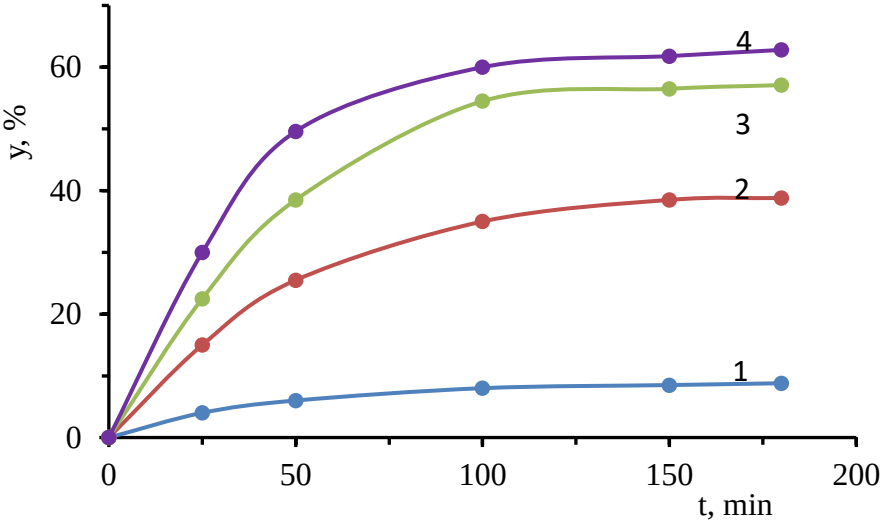


Fig. 6 Effect of initiator concentration on the yield of the DMAA-TMAPMACh copolymer. (Initiator concentration (mol/L): 0.05 (1); 0.07 (2); 0.1 (3) and 0.2 (4). [M]= 1 mol/L. Composition of the initial mixture [DMAA]:[TMAPMACh]= 50:50 mol. %. T = 333 K.)

The concentration of the initiator was changed from 0.05 to 0.2 wt. %. It was found that with an increase in the concentration of initiator by 4.0 times, the copolymer yield increased by 7.1 times (Table 5).

The dependence of the copolymerization reaction rate on the initiator concentration was calculated using equation (5):[74, 80, 81]

$$R_c = -\frac{d[I]}{dt} = [I]\frac{dy}{dt}. \quad (5)$$

where, [I] is an initiator concentration, mol/L; t is a time, min.; y is a copolymer yield, wt. %.

The value of dy/dt was determined from the slope of the initial portion of the curve y = f(t) (Fig. 6), corresponding to the different values of the initiator concentration. The Table 5 presents the results of the calculation using equation (5) and other parameters.

Now we can plot the dependence log R_c = f(log[I]) (Fig. 7) and from this figure we can obtain the equation describing the dependence of the copolymerization reaction rate on the initiator concentration: $R_c \propto [I]^{1.24}$.

Figure 8 shows the effect of monomer concentration on the copolymerization reaction rate (R_c). The reaction rate was calculated according to the equation (6):

$$R_c = -\frac{d[M]}{dt} = [M]\frac{dy}{dt}, \quad (6)$$

where, [M] is a total concentration of the monomers, mol/L; t is a time, min.; y is a copolymer yield, wt. %.

The value of dy/dt was determined from the slope of the initial portion of the curves y = f(t) (Fig. 8), corresponding to different values of the total concentration of monomers. Table 6 shows the copolymerization reaction rates calculated using equation (6) and other parameters.

From the table we can draw the following conclusion: with an increase in the total concentration of monomers by 4 times, the yield of copolymer increases by 7 times and the reaction rate increases by approximately 43 times. This can be explained as follows: with increasing concentration of monomers, the probability of the interaction of monomers with each other increases. This leads to an increase in the reaction rate.

Then you can plot the dependence log Rc = f(log[M]) (Fig. 9) and from that we can obtain the equation describing the dependence of the copolymerization reaction rate on the total concentration of the monomers: $R_c \propto [M]^{2.70}$.

Table 5. Effect of the initiator concentration on the yield of the DMAA-TMAPMACh copolymer. T = 333 K. [M] = 1 mol/L. The molar composition of the monomers in the initial mixture is [TMAPMACh]:[DMAA] = 50:50 mol. %. The initiator is $(NH_4)_2S_2O_8$.

[I], wt %	0.05	0.07	0.1	0.2
[I], mol/L	0.002	0.003	0.004	0.009
y(max), wt %	8.8	38.8	57.1	62.8
$\frac{dy}{dt}, min^{-1}$	0.20	0.68	1.00	1.35
$R_c = [M]\frac{dy}{dt}, mol/(L\cdot min)$	0.20	0.68	1.00	1.35
log [I]	-2.66	-2.51	-2.36	-2.06
log R_c	-0.70	-0.17	0.00	0.13

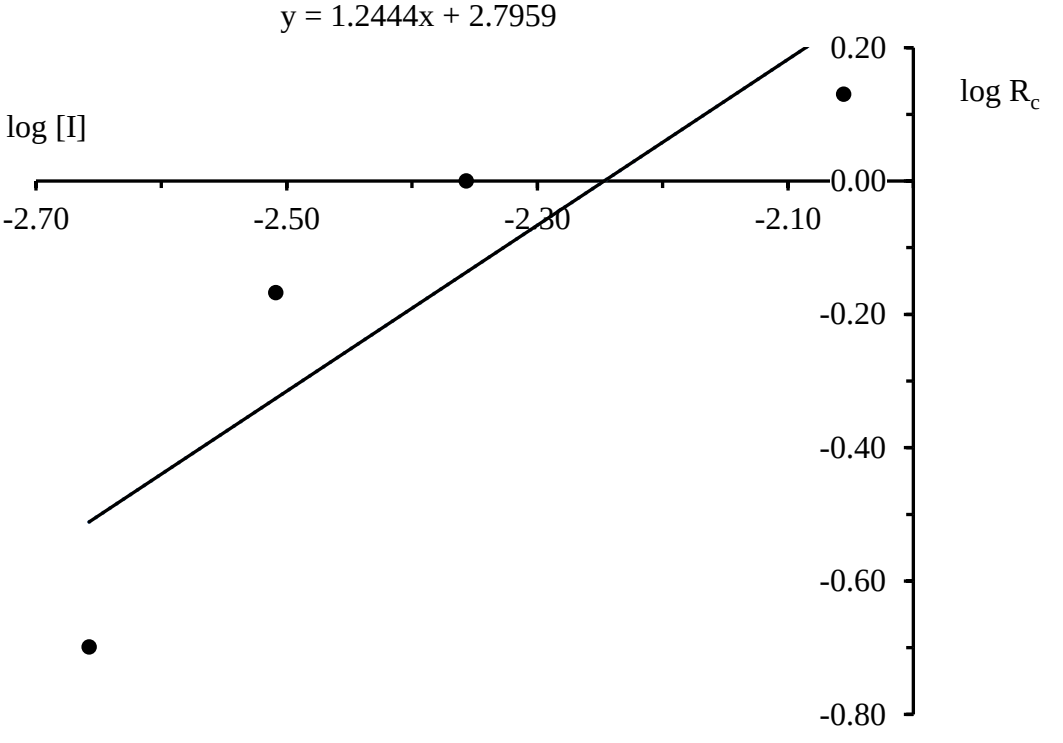


Fig. 7 Effect of the initiator concentration on the rate of copolymerization reaction in the system DMAA-TMAPMACh. (Composition of the initial mixture: [DMAA]:[TMAPMACh]=50:50 mol. %. [M] = 1 mol/L. T=333 K.)

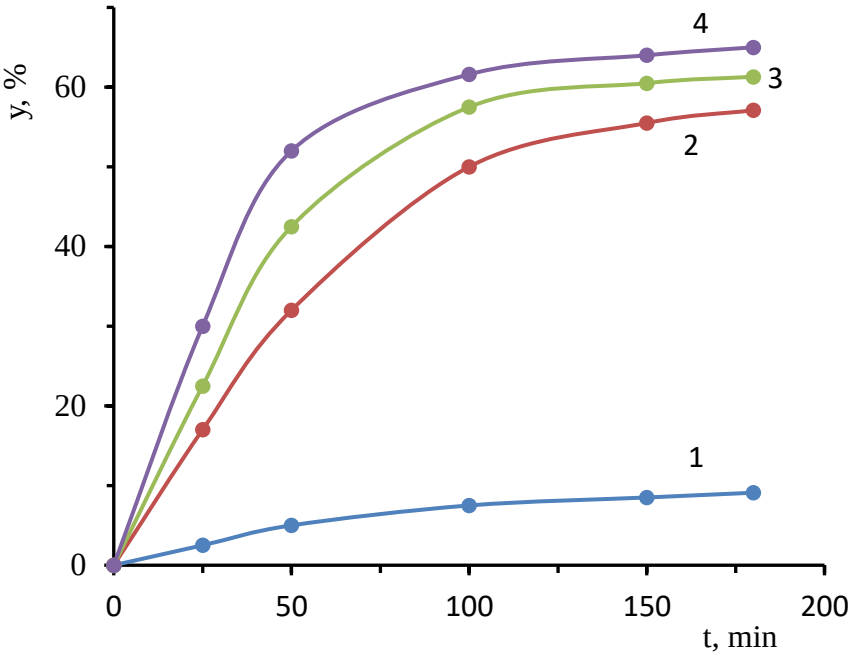


Fig. 8 Effect of the total concentration of monomers on the yield of the DMAA-TMAPMACh copolymer. (Total concentration of monomers (mol/L): 0.5 (1); 1.0 (2); 1.5 (3) and 2 (4). $[(NH_4)_2S_2O_8]$=0.5 wt %. Composition of the initial mixture: [DMAA]:[TMAPMACh]=50:50 mol. %. T=333 K.)

Table 6. Effect of the total concentration of monomers in the initial mixture on the yield of the DMAA-TMAPMACh copolymer. T = 333 K. $[(NH_4)_2S_2O_8]$ = 0.1 wt %. The molar composition of monomers in the mixture [DMAA]:[TMAPMACh] = 50: 50 mol. %.

[M], mol/L	0.5	1	1.5	2
y(max), wt %	9.2	57.1	61.3	62.8
$\frac{dy}{dt}$, min^{-1}	0.12	0.7	0.94	1.28
$R_c = [M]\frac{dy}{dt}$, mol/(L· min)	0.06	0.70	1.41	2.56
log R_c	-0.30	0.00	0.18	0.30
log [M]	-1.22	-0.15	0.15	0.41

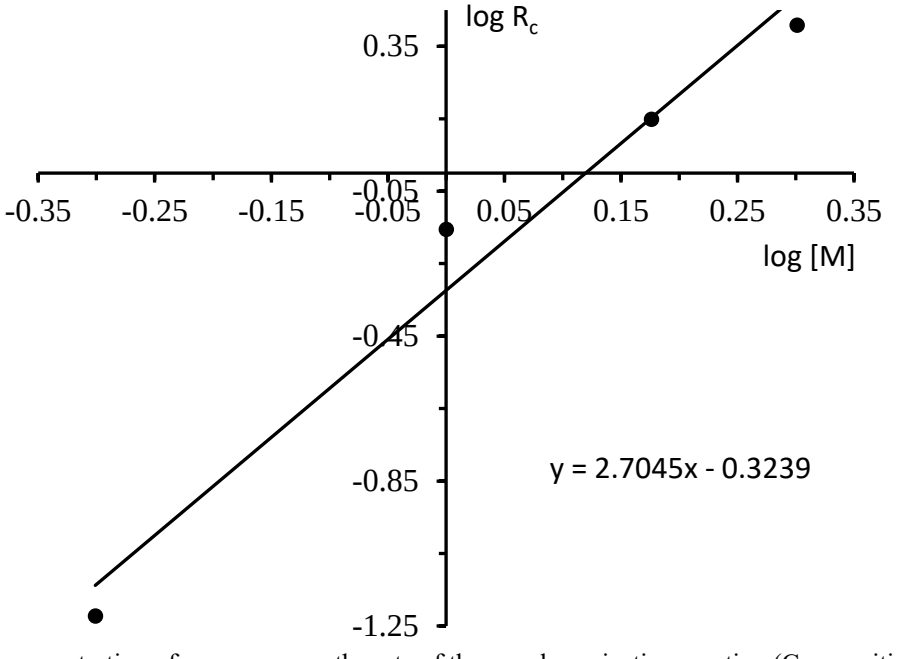


Fig. 9 Effect of the total concentration of monomers on the rate of the copolymerization reaction (Composition of the initial mixture [DMAA]:[TMAPMACh]=50:50 mol. %. $[(NH_4)_2S_2O_8]$ = 0.1 wt. %. T=333 K.).

Thus, the kinetic equation expressing the rate of the copolymerization reaction in the DMAA-TMAPMACh system (composition of the initial mixture [DMAA]:[TMAPMACh] = 50:50 mol. %) at a temperature T = 333 K is written as follows:

$$R_c = k\times [M]^{2.70}\times[I]^{1.24}, \quad (7)$$

where, k is the rate constant; [M] and [I] are the total concentration of monomers and the concentration of the initiator, respectively.

Now, using equation (7), we can calculate the rate constant (k) of the copolymerization reaction in the DMAA-TMAPMACh system.

1) From Table (6) under the condition [I] = 0.1 wt. % = 0.0044 mol/L = const and at monomer concentration [M] = 1.0 mol/L, the copolymerization reaction rate is R_c = 0.70 mol/(L×min). Then equation (7) is written as follows: 0.70 mol/(L×min)=k×[1.0 mol/L]$^{2.70}$×[0.0044 mol/L]$^{1.24}$.

From this equation we can calculate the rate constant:

$$k = \frac{0.70}{([1.0]^{2.70}\times[0.0044]^{1.24})} = \frac{0.70}{(1.0\times0.0012)} = 583.3\ \frac{L^{2.94}}{mol^{2.94}\times min} = 9.72\ \frac{L^{2.94}}{mol^{2.94}\times s}.$$

2) From Table 5 at [M]=1 mol/L =const and initiator concentration [I] = 0.1 wt. % = 0.044 mol/L, the reaction rate is R_c = 1.00 mol/(L×min). Then equation (7) is written as follows:

1.00 mol/(L×min) = k×[1 mol/L]$^{2.70}$×[0.0044 mol/L]$^{1.24}$.

If we find the rate constant from this equation:

$$k = \frac{1.00}{([1.00]^{2.70}\times[0.0044]^{1.24})} = \frac{1.00}{(1.00\times0{,}0012)} = 833.3\ \frac{L^{2.94}}{mol^{2.92}\times min} = 13{,}9\frac{L^{2.94}}{mol^{2.94}\times s}.$$

Consequently, the average rate constant for the reaction of radical copolymerization of the DMAA monomer with TMAPMACh in the presence of $(NH_4)_2S_2O_8$ at a temperature T=333 K is:

$$k_{av} = \frac{9.72 + 13.9}{2} = 11.8\ \frac{L^{2.94}}{mol^{2.94}\times s}.$$

In several studies it has been found that in the kinetic equation of the copolymerization reaction, the exponent of the total concentration of monomers is greater than 1.0. In the article [6], when studying the copolymerization reaction of N,N-diallyl-N,N-dimethylammonium chloride (DADMAC) with acrylamide (AA) at 45 °C in the presence of a mixture of APS and sodium bisulfate as an initiator, the following kinetic equation was obtained: $R_p = k\times[M]^{2.84}\times[I_O]^{0.51}\times[I_R]^{0.61}$ (where [M] is the total concentration of monomers, $[I_O]$ is the concentration of the oxidizing agent, $[I_R]$] is the concentration of the reducing agent).

Authors of [65], while studying the radical copolymerization reaction of DADMAC with vinyl ether of monoethanolamine (VEMEA) in the presence of APS (mixture composition [DADMAC]:[VEMEA] = 90:10 mol. %) at 65 °C obtained the following kinetic equation: $R_p = k\times[M]^{2.6}\times[I]^{0.6}$.

In [61] the authors studied the kinetics of the radical copolymerization reaction of DADMAC with dimethylacrylamide (DMAA) at 60 °C in the presence of APS as an initiator and obtained the following kinetic equation: $R_p = k\times[M]^{2.63}\times[I]^{0.40}$.

The kinetics of radical copolymerization of DADMAC with N-[3-(dimethylamino)propyl]-methacrylamide (DMAPMA) in an aqueous medium at 70 °C in the presence of APS was studied in [79]. Then the following kinetic equation was obtained for the DADMAC-DMAPMA copolymer: $R_c = k\times[M]^{3.48}\times[I]^{0.033}$.

In the work [81] the copolymerization rate equation for reaction of DADMAC with acrylamide (AA) initiated by $(NH_4)_2S_2O_8$ in aqueous solution at 55 ºC was obtained: $R_p=k[M]^{2.23}[I]^{0.70}$, where [DADMAC]:[AA] = 4:1.

We also obtained the kinetic equation for the copolymerization reaction in the mixture TMAPMACh with itaconic acid (IA) (composition of the initial mixture [TMAPMACh]:[IA] = 50:50 mol. %) at a temperature T = 343 K in the presence of APS: $R_c = k\times[M]^{1.66}\times[I]^{0.35}$[82]

3.6 Biocidal properties of DMAA-TMAPMACh copolymers

In order to determine the field of application, the biocidal properties of the synthesized copolymer against corrosion-damaging bacteria were studied.[20,27,39,79,83]

DMAA-TMAPMACh copolymer with different molar composition was tested as a biocidal material to inhibit the growth of sulfate-reducing bacteria (SRB) and thiobacterium Thiobacillus ferrooxidans (TB.[83] For testing, DMAA-TMAPMACh copolymers with a molar composition [TMAPMACh]:[DMAA] (mol. %) = 40:60 (1); 50:50 (2) and 60:40 (3) were taken. The effect of the samples of copolymers (1) and (2) on the growth of an enrichment culture of SRB and thionic bacteria Thiobacillus ferrooxidans was studied at eight concentrations (wt. %): 0.001; 0.005; 0.01; 0.05; 0.1; 0.2; 0.5 and 1.0, and for sample (3) – in five concentrations (wt. %): 0.001; 0.005; 0.01; 0.05 and 0.1.

The biocidal properties of the copolymers in relation to the SRB enrichment culture were determined by two methods:

1) 1 ml of SRB enrichment culture was added to the test tubes and filled with Postgate medium with a copolymer dissolved in the appropriate concentration to the full volume and closed with rubber stoppers to create anaerobic conditions. In the control variant (K) SRB was cultured without the copolymer. The tubes were placed in a thermostat for 15 days at a temperature of 30 °C.

2) 1 ml of SRB enrichment culture was added to test tubes, dosed with the studied concentrations of copolymers and topped up with sterile water to 20 ml, capped, and kept at room temperature for 24 hours. A tube with an enrichment culture without the addition of biocide served as a control sample. After exposure, 1 ml of liquid was taken from the test tubes,

introduced into sterile test tubes and filled with Postgate medium to the full volume and closed with rubber stoppers to create anaerobic conditions. The tubes were placed in a thermostat for 15 days at a temperature of 30 ℃.

The results of the study showed the absence of a bactericidal effect of the studied copolymers relative to SRB at concentrations of 0.001/0.1 wt. % (Fig. 10, 1-3). Copolymer samples (1) and (2) at concentrations of 0.2/1.0 wt. % delayed the development of SRB, but did not completely suppress their growth. Although the complete development of a black film with a metallic sheen (formation of iron sulfide) on the inner surface of the tube was not observed (Fig. 10, 1-2), microscopy showed the presence of bacterial cells.

Fig. 10 Growth of sulfate-reducing bacteria (SRB) in the presence of various concentrations of [TMAPMACh]:[DMAA] copolymers with different monomer ratios: (1) [TMAPMACh]:[DMAA] (mol.%) = 40:60; (2) [TMAPMACh]:[DMAA] (mol.%) = 50:50; (3) [TMAPMACh]:[DMAA] (mol.%) = 60:40. The rightmost sample, labeled as K, represents the control variant where SRB was cultured without the copolymer.

The biocidal properties of the copolymers against the thionic bacteria Thiobacillus ferrooxidans (TB) were also determined by two methods:

1) 1 ml of an enrichment culture of Thiobacillus ferrooxidans was added to the test tubes and 9 ml of K-9 nutrient medium with a copolymer dissolved in the appropriate concentration was poured. In the control variant (K), bacteria were cultivated without the copolymer. The tubes were placed in a thermostat for 15 days at a temperature of 30 ℃.

2) 1 ml of an enrichment culture of Thiobacillus ferrooxidans was added to test tubes, dosed with the studied concentrations of copolymers and topped up with sterile water to 10 ml, and kept at room temperature for 24 hours. A tube with an enrichment culture without the addition of biocide served as a control sample. After exposure, 1 ml of liquid was taken from the test tubes, introduced into sterile test tubes and filled with 9 ml of nutrient medium. The tubes were placed in a thermostat for 15 days at a temperature of 30 ℃.

Fig. 11 Growth of thionic bacteria Thiobacillus ferrooxidans in the presence of various concentrations of [TMAPMACh]:[DMAA] copolymers with different monomer ratios: (1) [TMAPMACh]:[DMAA] (mol.%) = 40:60; (2) [TMAPMACh]:[DMAA] (mol.%) = 50:50; (3) [TMAPMACh]:[DMAA] (mol.%) = 60:40. The rightmost sample, labeled as K, represents the control variant where SRB was cultured without the copolymer.

The results showed that samples of copolymers (1) and (2) had a bactericidal effect against the bacteria Thiobacillus ferrooxidans at a concentration of 1 wt % (Fig. 11).

At a concentration of 0.2 wt % and 0.5 wt. %, complete inhibition of growth was not observed, but only a delay in their development. At a concentration of 0.001÷0.1 wt %, all samples showed no bactericidal effect on thionic bacteria (Fig. 11).

We can conclude that the provided samples of copolymers DMAA-TMAPMACh with molar composition [TMAPMACh]:[DMAA] (mol. %) = 40:60 and 50:50 have biocidal effects against thionic bacteria at a minimum concentration of 1.0 wt. %. They do not have a bactericidal effect on the growth of sulfate-reducing bacteria, but they cause a delay in their development at a concentration of 0.2/1.0 wt. %. Thus, bactericidal effects of synthesized polymers showed similar even better results than similar works done by other scientists.[84,85]

Further, in order to determine the areas of application flocculating,[62,80,86] surface (adsorption)[87] and complex formation[88,89] properties of the DMAA-TMAPMACh copolymers will be studied.

4. Conclusions

1. A cationic DMAA-TMAPMACh copolymer with different molar composition was synthesized at T=333 K by free radical copolymerization in the presence of $(NH_4)_2S_2O_8$ as an initiator.
2. The functional and molar compositions of the synthesized copolymers were determined by IR and ^{1}H NMR spectroscopy and conductometric titration.
3. The influence of the concentration of monomers and initiator on the yield of the copolymer was studied. It was found that as the total concentration of monomers in the initial mixture and the concentration of the initiator increase, the yield of the DMAA-TMAPMACh copolymer rises. The kinetic equation for the DMAA-TMAPMACh system (composition of the initial mixture [DMAA]:[TMAPMACh]=50:50 mol. %) at temperature T=333 K was written as follows: $R_c = k\times [M]^{2.70}\times[I]^{1.24}$.
4. The relative activity coefficients of monomers were calculated by using the Mayo-Lewis and Fineman-Ross equations. It was found that in the radical copolymerization reaction the DMAA monomer is more active than the TMAPMACh monomer. For this reason, the molar concentration of the DMAA monomer in the synthesized copolymer is always greater than that in the initial monomers' mixture.
5. The biocidal properties of the DMAA-TMAPMACh copolymer against SRB bacteria and thionic bacteria Thiobacillus ferrooxidans (TB) were determined. It has been established that copolymers with the molar composition [TMAPMACh]:[DMAA] (mol. %) = 40:60 and 50:50 have biocidal properties against TB at a minimum concentration of 1.0 wt. %. They do not have a bactericidal effect against SRB bacteria, but they cause a delay in their development at a concentration of 0.2/1.0 wt. %.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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