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A Polyampholyte Based on Itaconic Acid And [(3-Methacryloylamino)Propyl]-Trimethylammonium Chloride: Synthesis and Study of Biocidal Properties

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Abstract

In this work, a copolymer of [(3-methacryloylamino)propyl]trimethylammonium chloride (TMAPMACh) and itaconic acid (IA) with different molar composition was synthesized by the method of free radical copolymerization in an aqueous medium in the presence of an initiator (ammonium persulfate, $(NH_4)_2S_2O_8$). The functional and molar composition of the synthesized copolymers was determined by the methods of elemental analysis, conductometric titration, Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR). Coefficients of monomer reactivity were determined using Mayo-Lewis ($r_{TMAPMACh}$=0.50±0.02 and r_{IA}=1.50±0.02) and Fineman-Ross ($r_{TMAPMACh}$=0.44±0.02 and r_{IA}=1.51±0.02) methods. It is established that in the radical copolymerization reaction, monomer IA is more reactive than monomer TMAPMACh, and copolymers with a more statistically uniform distribution of monomer units along the macromolecule chain are formed. The influence of the concentration of monomers [M] and initiator [I] on the rate of copolymerization reaction (R_c) at 343 K and equimolar ratios of monomers in the initial mixture was investigated. The kinetic equation of copolymerization reaction in a mixture of TMAPMACh with IA was obtained: $R_C = k \times [M]^{1.66} \times [I]^{0.35}$. The average rate constant of the copolymerization reaction for this temperature was $k = 0{,}049 \times L^{0.92} \times mol^{-0.92} \times s^{-1}$. The results of the copolymerization reaction kinetics make it possible to regulate the process of copolymer formation and thereby obtain a polymer surfactant with the required physicochemical properties. The TMAPMACh-IA copolymer has a biocidal effect against sulfate-reducing bacteria (SRB), and therefore can be used to suppress the growth of this bacteria.

Keywords: Free radical polymerization; Itaconic acid; Biocidal polymer; Microbiological corrosion.
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1. Introduction

Itaconic acid (2-methylene succinic acid) is an unsaturated weak dicarboxylic acid (pKa=3.84 and 5.55 at 25 °C), which was first obtained by S. Baup in 1837 during the thermal distillation of citric acid.[1-3] Currently, in industry, itaconic acid is mainly produced by fermentation of carbohydrates (glucose, molasses and unrefined starch hydrolyzate) using fungi such as Aspergillus itaconicus[4] and Aspergillus terreus.[5]

Itaconic acid (IA) dissolves well in water, ethanol and acetone. IA resembles acrylic acid in its molecular structure. Due to the presence of a conjugated double bond in the structure, IA can participate in radical polymerization reactions with various vinyl monomers. It is also possible to carry out the reaction of esterification of two carboxylic acid groups with different monomers.[6] In addition, IA has antimicrobial, anti-inflammatory and anti-tumor activity. Recently, IA is produced on an industrial scale using biotechnological methods.[7-10]

The growing interest in IA is due to the desire of the world community to replace chemicals derived from petroleum with

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environmentally safer substances produced from renewable sources of raw materials. For this reason, the US Department of Energy lists itaconic acid as one of the 12 compounds with the highest potential,[11,12] which can be produced from biomass of beech wood,[13] corn stover,[14] wheat chaff,[15] rice husks[16] and corn cobs[17] or biological waste.[18,19] In 2023, global production of itaconic acid was approximately 204.6 million US dollars.[20]

Due to the difficulty of radical homopolymerization of the monomer, IA was not of commercial interest for many years. However, today the situation is completely different. Currently, itaconic anhydride (or itaconic acid) is widely used in industry as a comonomer for the production of rubber materials, paints and dyes, coatings, biodegradable polymers, contact lenses and other medical applications.[21,22]

Ithaconic anhydride (IAn) has been also used as a monomer with various vinyl monomers[23-25] and styrene.[26] The largest producers of itaconic acid are the USA, China, Japan, Germany, India and others.[27]

Polymers and copolymers based on IA can be obtained by the free radical polymerization reaction.[28-33] In Ref. [34], copolymerization of diallylamine (DAA) and itaconic acid was carried out in a nitrogen atmosphere by free radical polymerization using benzoyl peroxide as an initiator. The composition of the copolymer was determined by its nitrogen content using Edx. The structure of the copolymer was proven by ^{13}C-NMR spectroscopy. In order to improve the solubility of copolymers in water and increase their hydrophilicity, the copolymers were allowed to react with chitosan to form a superabsorbent. It was found that during the radical copolymerization reaction, DAA forms polymer branches in the form of five-membered pyrrolidone rings, while itaconic acid forms condensation products with the amino group of chitosan and the NH group of pyrrolidone rings. It has also been shown that the superabsorbent has good thermal stability compared to native chitosan. In this case, an increase in the percentage of itaconic acid leads to an increase in water absorption of the absorbent. Moreover, the polymer superabsorbent demonstrated superior water retention efficiency compared to native chitosan, retaining up to 50% water after 40 hours. The high-water absorption capacity of the copolymer, which includes itaconic acid, is explained by the ability of the acid to form hydrogen bonds with water molecules.

A cross-linked copolymer of itaconic anhydride (IAn) with methyl methacrylate (MMA) was synthesized by free radical copolymerization using microwave irradiation in the presence of azobisisobutyronitrile as an initiator and 2-butanone as a solvent.[35] The copolymerization process was carried out in the presence of two types of crosslinking agent, namely ethylene dimethacrylate (EDMA) and divinylbenzene (DVB) in the range of 0÷20 wt%. It was found that the morphological structure is influenced by the ratio of monomers and the type of cross-linking agent used. As the proportion of cross-linking agent increases, the copolymers precipitate and do not form a gel during polymerization. An increase in the amount of MMA in the copolymer leads to the formation of a cross-linked copolymer rather than a gel. When EDMA is used as a cross-linking agent, the copolymers change structure, from porous to rigid, depending on the molar ratio of monomers in the mixture. On the other hand, when using DVB as a cross-linker, the stiffness structure was obtained in all cases and no influence of the monomer ratio or percentage of cross-linker on the morphology of the resulting copolymers was observed. The synthesized copolymers demonstrated high thermal stability. Moreover, the thermal stability of the IA-MMA copolymer increased with increasing IA content. In general, stiffness patterns of the copolymers were observed with increasing percentage of crosslinker used.

In Ref. [36], a new environmentally friendly scale inhibitor was synthesized by free radical polymerization of itaconic acid, acrylamide (AA) and p-styrene sodium sulfonate (SSS). Synthesis conditions such as monomer ratio, initiator dosage, titration time and reaction temperature were optimized by static scale inhibition method, and a polymer scale inhibitor was obtained. The results showed that the copolymer had good ability to control calcium carbonate deposits, and the inhibition rate of $CaCO_3$ reached 84.7% at a dose of 30 mg/L. Using microscopic morphology, it was found that the copolymer can change the crystallization path of calcium carbonate from stable calcite to witherite. The proposed inhibition mechanism suggests that surface complexation between the functional groups of the copolymer and Ca^{2+} results in superior solubility of the complexes. These results suggested that the resulting copolymers had great potential for application in oil fields for scaling inhibition.

In Ref. [37], a biodegradable hydrogel nanocomposite (HNC) based on starch, gelatin, itaconic and acrylic acids was obtained in the presence of cellulose nanofibers and zinc oxide (CNF/ZnO), which can be used for controlled drug delivery applications. The addition of nanohybrid (CNF/ZnO) has been shown to improve the porosity and swelling ability of the hydrogel. Moreover, a sustained drug release rate was observed at pH 4, indicating controlled release and pH-dependent behavior of HNC. It was also found that the released HNC drug can be reused as a photocatalyst for dye degradation. The antibacterial activity of HNC against Escherichia coli (EC) and Staphylococcus aureus (SA) bacterial strains was confirmed in an antibacterial test. The authors concluded that HNC can be considered an effective sustained drug delivery system (DDS) for biomedical applications, as well as a photocatalyst for water purification from dyes.

The goal of this work is to synthesize a polyampholytic surfactant from available industrial monomers. This polymer surfactant can be used as a flocculant for the purification of natural and industrial wastewater from metal ions and highly dispersed pollutant particles,[38,39] as a bactericidal (biocidal) compound to suppress the growth of microorganisms and bacteria,[40-42] as a structure former to regulate the viscosity of

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suspensions and clay drilling fluids[43] and as a complexing agent to regulate the surface properties of surfactants and water-soluble polymers.[44,45]

The presence of two negatively charged carboxyl groups in TMAPMACh-IA copolymer allows polymer macromolecules to interact with positively charged dispersed particles of the suspension to flocculate them, interact with cationic surfactants to form a complex, and desalinize wastewater by interacting with metal cations in solution.

While the positively charged quaternary ammonium group in TMAPMACh-IA copolymer allows polymer macromolecules to interact with negatively charged dispersed particles of the suspension to flocculate them, interact with anionic surfactants to form a complex, and undergo an ion exchange reaction with electrolyte anions, therefore allowing to purify of wastewater from harmful ions. Moreover, both functional groups have bactericidal (biocidal) properties.

2. Experimental

2.1 Materials

Itaconic acid (IA) was obtained by hydrolysis of itaconic anhydride (IAn). IAn from Sigma Aldrich (purity: not less than 98 wt%) was used. [(3-methacryloylamino)propyl]trimethylammonium chloride (TMAPMACh) was used as a 95 wt% solution in water (Sigma Aldrich Ltd.). Ammonium persulfate ($(NH_4)_2S_2O_8$), purity 99.7 wt%) was purchased from LaborPharma Ltd. (Almaty, Kazakhstan). Acetone was purchased from Sigma Aldrich Ltd. (purity 99.9%). Argon gas (purity 99.995 wt%) was kindly provided by IkhsanTechGas (Almaty, Kazakhstan). In all experiments distilled water with a conductivity 2.4 μS/cm at 20 °C was used.

2.2 Methods

The functional and molar compositions of the copolymers were determined by IR and NMR spectroscopy, elemental analysis, and conductometric titration of the chloride anions of the copolymer with an $AgNO_3$ solution.

The IR spectrum of the TMAPMACh-IA copolymer sample was recorded on a Nicolet 5700 spectrometer, Termo Corporation, USA in the frequency range 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 was recorded on a JNM-ECA Jeol 400 spectrometer (frequency 399.78 and 100.53 MHz, respectively) at 20 °C using D_2O as a solvent. The NMR spectrum of the copolymer synthesized from the mixture [TMAPMACh]:[IA]=40:60 mol % was recorded. Chemical shifts were measured relative to the residual proton signals of the deuterated solvent.

Elemental analysis for the nitrogen atom in the copolymer was carried out on a Vario EL Cuba installation (Germany).

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

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

The viscosity of the copolymer solution was determined at room temperature using an Ubellode viscometer.[46] The relative viscosity (η_r) of the copolymer is calculated according to the equation:

$$\eta_r = \frac{\eta_c}{\eta_w} = \frac{\tau_c}{\tau_w},$$

where η_c and η_w are the viscosity of the copolymer solution and the solvent (water), respectively; τ_c and τ_w – flow time of the copolymer solution and solvent (water), respectively.

The specific viscosity (η_{sp}) of the copolymer solution is calculated using the equation:

$$\eta_{sp} = \frac{\eta_c - \eta_w}{\eta_w} = \frac{\tau_c - \tau_w}{\tau_w}.$$

The reduced viscosity (η_{red}) of the copolymer solution is determined according to the equation:

$$\eta_{red} = \frac{\eta_{sp}}{c},$$

where c is the concentration of the copolymer solution, g/dl.

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

$y = m_{cop} \times 100\%/m_{mon}$,

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

The biocidal properties of the TMAPMACh-IA copolymer with different molar compositions against the growth of sulfate-reducing bacteria (SRB) 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 is 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.[46] At a selected temperature, copolymerization is carried out for each total concentration of monomers, and the copolymer yield is determined at certain time intervals. Then, based on the obtained data, a graph of the copolymer yield dependence on the copolymerization reaction duration is constructed. The rate of the copolymerization reaction for each concentration is determined (R_c(mol/(L×min) from the slope of the initial portion of the curves "yield versus time" (y = f(t)). After this, 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) is equal to the order of the copolymerization reaction by monomer.[46]

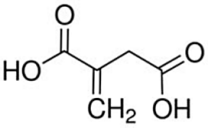
To determine the reaction order *by initiator*, copolymerization is carried out in a constant volume of solution, a constant concentration of the monomers in the solution, a constant molar ratio of monomers (for example,

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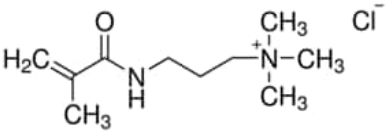
50:50 mol%) and a different concentration of initiator.[46] At a selected temperature, copolymerization is carried out for each initiator concentration, and the copolymer yield is determined at certain time intervals. Then, based on the obtained data, a graph of the copolymer yield dependence on the copolymerization reaction duration is constructed. The rate of the copolymerization reaction for each initiator concentration is determined (R_c(mol/(L×min) from the slope of the initial portion of the curves "yield versus time" (y = f(t)). After this, a graph of log R_c versus log [I] is plotted ([I] is the concentration of the initiator, mol/L). The slope of the resulting straight line (tgα) is equal to the order of the copolymerization reaction by initiator.[46]

2.4 Synthesis of copolymers

For the synthesis of the ampholytic copolymer, the monomers [3-(methacryloylamino)-propyl]trimethylammonium chloride (TMAPMACh) and itaconic acid (IA) were chosen:



IA



TMAPMACh

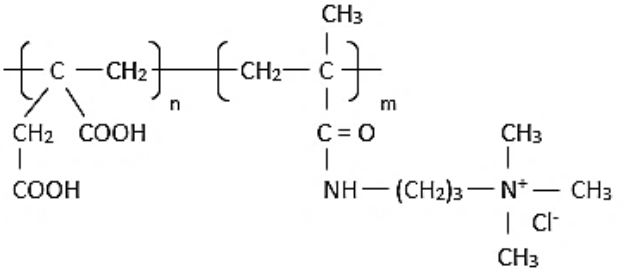
The main reasons for choosing these monomers are:

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

2) IA dissociates in an aqueous environment and becomes negatively charged, while the TMAPMACh monomer has a positive charge. Then the synthesized copolymer will exhibit the properties of a polyampholyte. In addition, the IA monomer has bactericidal properties, which enhances the biocidal effect of the TMAPMACh-IA copolymer. Secondly, the presence of simultaneously positively and negatively charged functional groups in the copolymer ensures electrostatic interaction of copolymer macromolecules with positively and negatively charged groups on the surface layer of microorganisms (colloidal and dispersed particles). While the hydrophobic properties of monomers enhance the hydrophobic interaction of the polyampholyte with the surface of the microorganism. Copolymers TMAPMACh-IA with structural formulawere synthesized in ampoules by the method of 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 water. After this, in order to remove oxygen, the mixture was purged with an inert gas (argon) for 15 minutes and the ampoule was immediately sealed. The ampoule with the reaction mixture was placed in a thermostat and heated at a temperature of 343 K for 3 hours.

Ammonium persulfate (APS), $(NH_4)_2S_2O_8$, was used as an initiator. The initiator concentration was varied in the range of 0.2÷1.0 wt% based on the mass of monomers. The total concentration of monomers was varied in the range of 1.0÷3.0 mol/L.

Then, 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 synthesized copolymers are white amorphous substances that are highly soluble in water.



3. Results and discussion

In this work, the influence of the molar composition of the initial monomer mixture on the composition and yield of the resulting copolymer was studied. Table 1 presents the results of the study.

Table 1. Effect of the molar ratio of monomers in the initial mixture on the composition and yield of the TMAPMACh-IA copolymer. [M] = 2 mol/L. [I] = 0.5 wt%.

Composition of the initial mixture, mol.%	The molar composition of the copolymer, determined by the conductometric method, mol.%	Molar composition of the copolymer, determined by elemental analysis (by nitrogen atom), mol.%	Yield of copolymer, wt%
[TMAPMACh]:[IA]	[TMAPMACh]:[IA]	[TMAPMACh]:[IA]	
80:20	67:33	64:36	84.1
60:40	42:58	43:57	82.3
50:50	41:59	38:62	79.8
40:60	32:68	31:69	73.1
20:80	11:89	10:90	54.5

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From the table data it is clear that with an increase in the mole fraction of the TMAPMACh monomer in the initial mixture, the yield of the copolymer increases. In this case, the molar amount of IA monomer in the synthesized copolymers is always greater than that in the original monomers' mixture. Therefore, we can conclude that the IA monomer is more active in the radical copolymerization reaction compared to the TMAPMACh monomer.

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

3.1 Analysis of the IR spectrum of the TMAPMACh-IA copolymer

The IR spectrum (Fig. 1) contains a band corresponding to the carboxyl group –COOH at 1726 cm^{-1}. At 2969 cm^{-1} a band corresponding to the bound hydroxyl group –OH is detected. The band corresponding to the free hydroxyl group is located at 3588 cm^{-1} and the band belonging to the secondary amide –CONHR is visible at 3304 cm^{-1}. There is also a band at 1644 cm^{-1}, corresponding to the carbonyl group C=O in the secondary amide (Amide I band). At a frequency of 1533 cm^{-1}, bands of bending vibrations are visible, corresponding to N–H and C–N bonds (Amide II band).[47,48] Therefore, based on the IR spectrum, it can be assumed that the synthesized copolymer contains both TMAPMACh and IA monomers.

3.2 Analysis of the ^{1}H NMR spectrum of the TMAPMACh-IA copolymer in D_2O

In the ^{1}H NMR spectrum of the TMAPMACh-IA copolymer (Fig. 2), one elongated singlet is visible at a chemical shift (ppm) of 0.76-0.90 (13.65H), a multiplet at a chemical shift of 1.71–1.82 (20.51H), singlet signal at a chemical shift of 2.01 (26.88H) and multiplet signals at a chemical shift of 2.94–3.16 (119.73H).[48] These spectra contain protons of TMAPMACh and IA fragment structures.

In the first extended singlet part of the spectrum 0.76-0.90 ppm. in the chemical shift, the protons of the methylene group of the H_f chain of the copolymer and the protons of the methyl group of the H_f of the TMAPMACh fragment are visible.

Methylene protons H_s, H_t and H_q of the TMAPMACh fragment are detected in the second multiplet signal at a level of 1.71–1.82 ppm. in a chemical shift. The H_c protons of the IA fragment are visible in the third singlet signal at a shift of 2.01 ppm. At a shift of 2.94–3.16 ppm. The most intense multiplet signal contains the H_w and H_v protons of the TMAPMACh fragment and the H_c and H_b protons of the IA fragment. The carboxyl protons H_e and H_o of the IA fragment participate in exchange processes with deuterated solvent molecules, and at a shift of 4.65 ppm. are visible along with the deuterated water signal.

To determine the composition of the TMAPMACh-IA copolymer, the integral proton intensity corresponding to one hydrogen atom in the IA fragment was determined. The integrated intensity of 2 protons H_c of the IA fragment is equal to 26.88 H. Hence, if we calculate the average intensity of the protons of one hydrogen atom in the IA fragment, it will be equal to: 26.88:2 = 13.44 H.

In the first extended singlet part of the spectrum 0.76–0.90 ppm. in the chemical shift, the protons of the methylene group of the H_f chain of the copolymer and the protons of the methyl group of the H_f of the TMAPMACh fragment are visible.

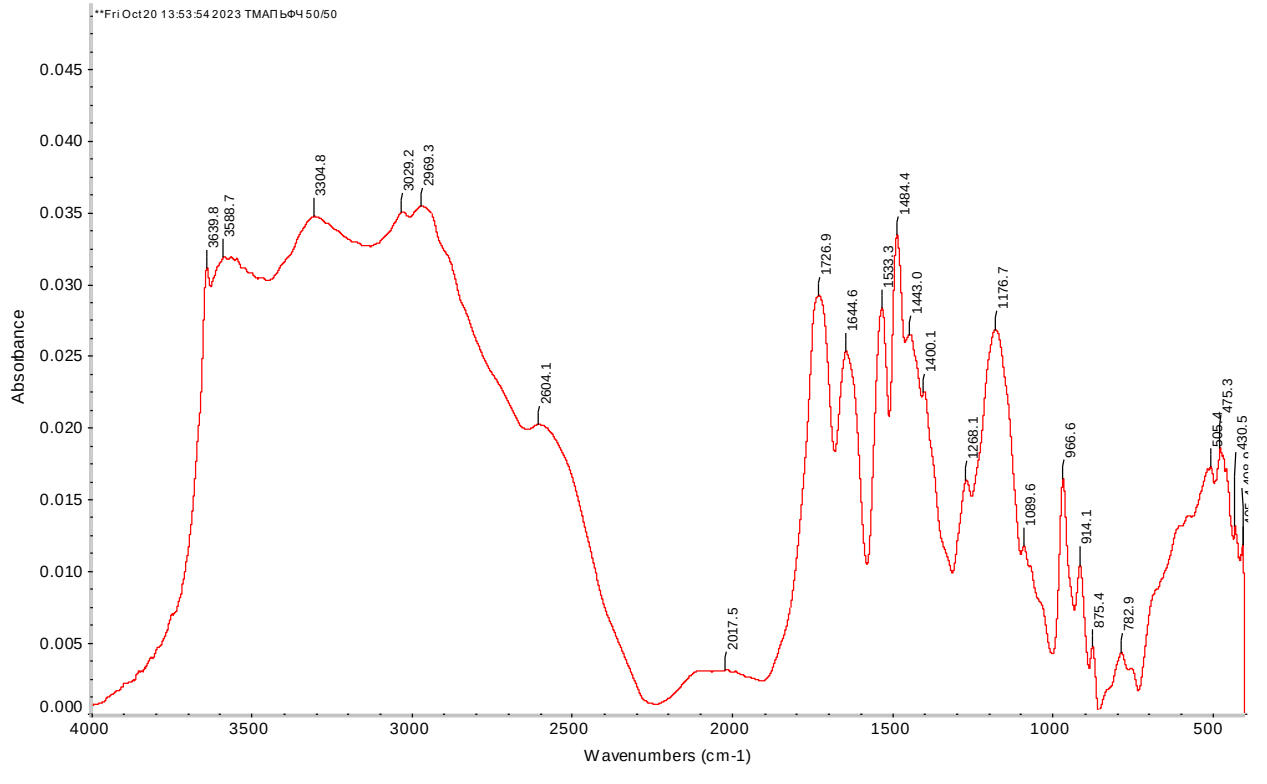
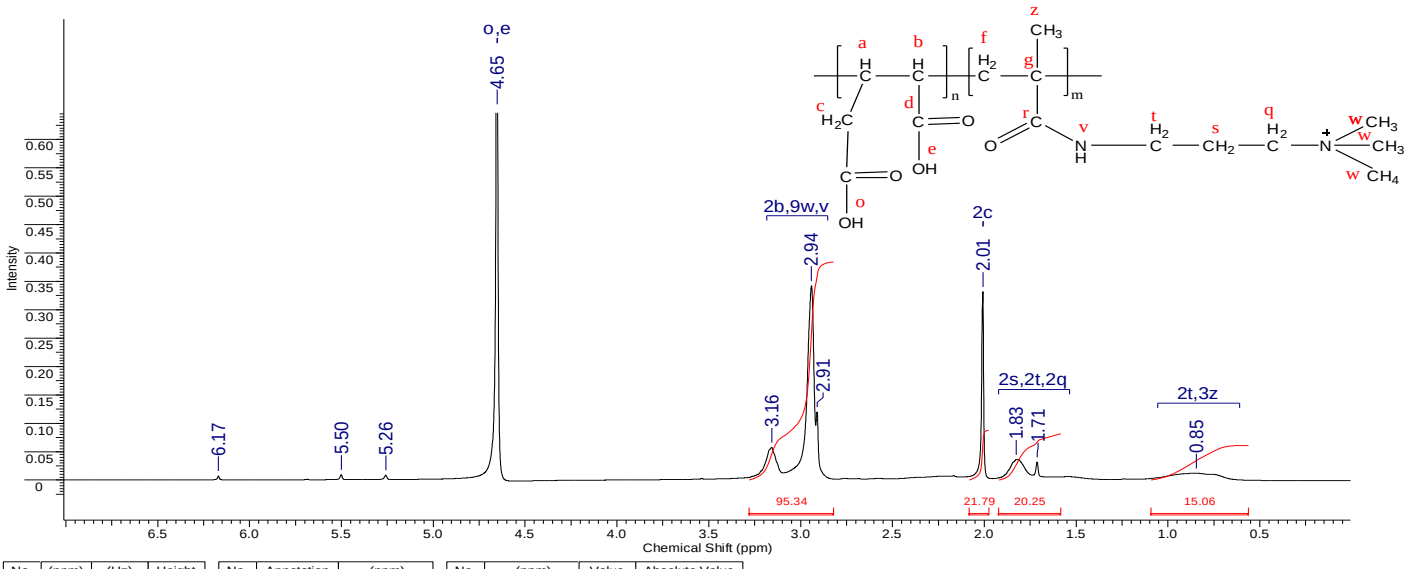


Fig. 1 IR spectrum of the TMAPMACh-IA copolymer.

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No.	(ppm)	(Hz)	Height
1	0.85	337.9	0.0120
2	1.71	684.6	0.0318
3	1.83	729.9	0.0360
4	2.01	802.3	0.3315
5	2.91	1163.6	0.1199
6	2.94	1176.0	0.3424
7	3.16	1262.1	0.0578
8	4.65	1860.2	1.0000
9	5.26	2101.9	0.0085
10	5.50	2199.0	0.0093
11	6.17	2466.5	0.0071

No.	Annotation	(ppm)
1	2t,3z	[0.61 .. 1.05]
2	2s,2t,2q	[1.54 .. 1.92]
3	2c	2.01
4	2b,9w,v	[2.85 .. 3.18]
5	o,e	4.65

No.	(ppm)	Value	Absolute Value
1	[0.56 .. 1.09]	15.062	2.00178e+1
2	[1.58 .. 1.92]	20.253	2.69172e+1
3	[1.97 .. 2.08]	21.787	2.89558e+1
4	[2.82 .. 3.28]	95.337	1.26708e+2

Fig. 2 1H NMR spectra of the TMAPMACh-IA copolymer in D2O.

Methylene protons H_s, H_t and H_q of the TMAPMACh fragment are detected in the second multiplet signal at a level of 1.71–1.82 ppm. in a chemical shift. The H_c protons of the IA fragment are visible in the third singlet signal at a shift of 2.01 ppm.

At a shift of 2.94–3.16 ppm. the most intense multiplet signal contains the H_w and H_v protons of the TMAPMACh fragment and the H_c and H_b protons of the IA fragment. The carboxyl protons H_e and H_o of the IA fragment participate in exchange processes with deuterated solvent molecules, and at a shift of 4.65 ppm. are visible along with the deuterated water signal.

To determine the composition of the TMAPMACh-IA copolymer, the integral proton intensity corresponding to one hydrogen atom in the IR fragment was determined. The integrated intensity of 2 protons H_c of the IA fragment is equal to 26.88 H. Hence, if we calculate the average intensity of the protons of one hydrogen atom in the IA fragment, it will be equal to: 26.88:2 = 13.44H.

The total intensity of the protons H_f, H_z, H_t, H_q, H_s, H_v and H_b is 13.65 + 20.51 + 119.73 = 153.89H. To determine the total integrated intensity of protons of the TMAPMACh fragment, it is necessary to subtract 26.88 H from 153.89 H, corresponding to 2 H_b protons, and it will be equal to 127.01H. It follows that the average intensity of protons of one hydrogen atom in the TMAPMACh fragment is 127.01:21 = 6.05H.
Then the composition of the TMAPMACh-IA copolymer will be equal to: 6.05H:13.44H = 1:2.22 or approximately 5:11 mol:mol.

Thus, the composition of the copolymer synthesized from the mixture [TMAPMACh]:[IA] = 40:60 mol. % copolymer is 31:69 mol. %. This is very close to the composition (32:68) determined by conductometric titration (Table 1).

3.3 Calculation of the relative reactivity of monomers

A quantitative characteristic of the reactivity of monomers is the copolymerization constants or their reactivity coefficients. Thus, the reactivity coefficients of the monomers (r_1 and r_2) were calculated from experimental data (Table 1) using the Mayo-Lewis (1) and Fineman-Ross (2) equations.[49,50]

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

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

$$F = [M_1] / [M_2]; \quad f = [m_1] / [m_2], \quad (3)$$

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

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

Sample serial number	The mole fraction of monomers in the initial mixture, mol.%		The mole fraction of monomers in copolymer, mol.%		Copolymer yield y, 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 (IA)	m_1 (TMAPMACh)	m_2 (IA)						
1	80	20	67	33	84.1	4.00	2.02	$r_2 = 7.92\times r_1 - 2.02$		
2	60	40	42	58	82.3	1.50	0.73	$r_2 = 3.08\times r_1 + 0.55$		
3	50	50	41	59	79.8	1.00	0.69	$r_2 = 1.455\times r_1 + 0.45$	0.50± 0.2	1.50± 0.2
4	40	60	32	68	73.1	0.67	0.47	$r_2 = 0.96\times r_1 + 0.76$		
5	20	80	11	89	54.5	0.25	0.13	$r_2 = 0.48\times r_1 + 1.67$		

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

Sample serial number	The mole fraction of monomers in the initial mixture, mol.%		The mole fraction of monomers in copolymer, mol.%		Copolymer yield y, wt%	F = $[M_1]/[M_2]$	f = $[m_1]/[m_2]$	x = (F^2/f)	y = $(F/f)\times(f-1)$	r_1	r_2
	M_1 (TMAPMACh)	M_2 (IA)	m_1 (TMAPMACh)	m_2 (IA)							
1	80	20	67	33	84.1	4.00	2.02	7.9	2.0		
2	60	40	42	58	82.3	1.50	0.73	3.1	-0.6		
3	50	50	41	59	79.8	1.00	0.69	1.5	-0.5	0.44±0.2	1.51±0.2
4	40	60	32	68	73.1	0.67	0.47	0.9	-0.8		
5	20	80	11	89	54.5	0.25	0.13	0.5	-1.7		

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

Method	r_1	r_2	$1/r_1$	$1/r_2$	$r_1\times r_2$
Mayo-Lewis	0.50	1.50	2.00	0.67	0.75
Fineman-Ross	0.44	1.51	2.27	0.66	0.66

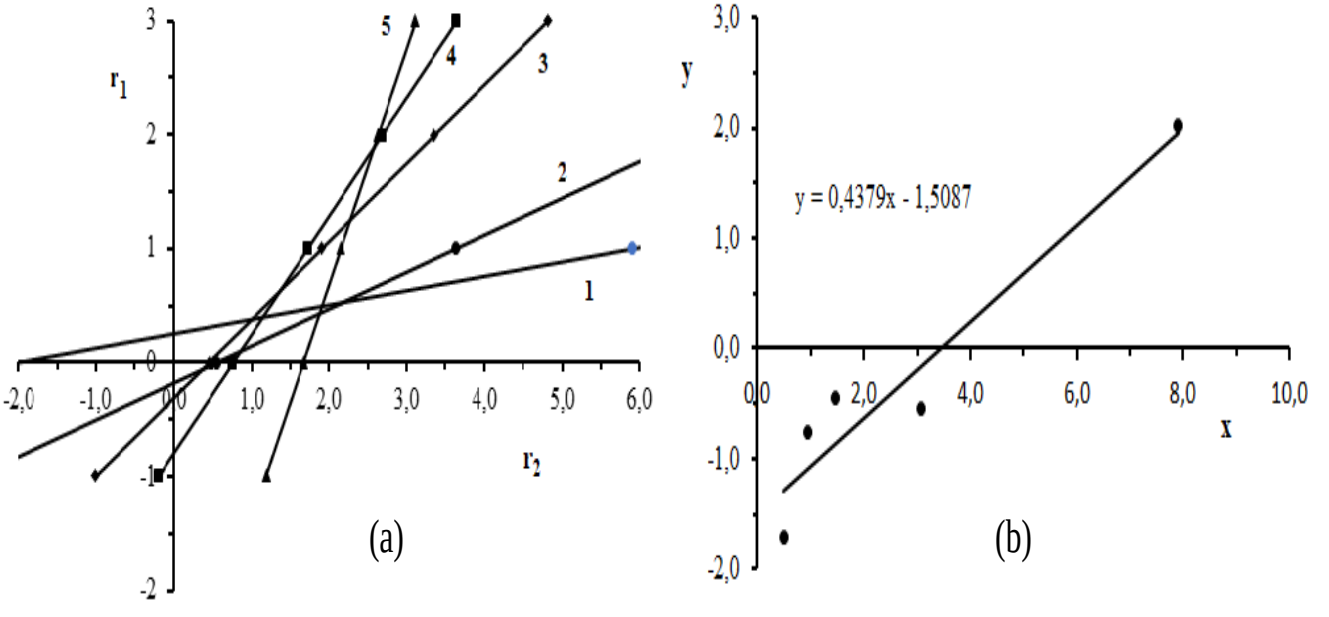


Fig. 3 Calculation of the reactivity coefficients of monomers in the TMAPMACh-IA system from graphs using the Mayo-Lewis (a) and Fineman-Ross (b) methods. Composition of the initial mixtures [TMAPMACh]:[IA] = 80:20 (1); 60:40 (2); 50:50 (3); 40:60 (4) and 20:80 (5).

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The reactivity coefficients of the monomers were determined from the graphs and entered into tables. The reactivity coefficients of the monomers TMAPMACh (1) and IA (2), calculated by various methods, are given in Table 4.

The reactivity coefficients calculated by different methods are close in value, and their multiplication is less than one. This indicates that during the reaction, copolymers with a more statistically uniform distribution of monomer units along the macromolecule chain are formed.[49,50] It should also be noted that the IA activity coefficient calculated by two indicated methods (1.50 and 1.51) is higher than that of TMAPMACh (0.50 and 0.44).

A comparison of the inverse values of the monomers' reactivity coefficients showed that macrochains ending with TMAPMACh units readily attach an "alien" monomer (IA) rather than the "native" one, while macrochains ending with IA units readily attach the "native" monomer rather than the "alien" one (TMAPMACh). For this reason, the TMAPMACh-IA copolymer is enriched with IA units.

The relatively weak reactivity of the TMAPMACh monomer in the radical copolymerization reaction is apparently due to the presence of a positive charge in the monomer structure and its bulk structure (steric effect). Mutual repulsion of like-charged particles makes it difficult to attach the TMAPMACh monomer to a macroradical with a terminal positive charge.

In this work, the effect of the total concentration of monomers on the yield of the copolymer was also studied (Fig. 4). It was found that with an increase in the total concentration of monomers by 3 times, the yield of the copolymer increases by 1.7 times (Table 5).

Figure 5 shows the effect of monomer concentration on the copolymerization reaction rate (R_c). The reaction rate was calculated according to the following equation (4):

$$R_c = -\frac{d[M]}{dt} = [M]\frac{dy}{dt}, \quad (4)$$

where [M] is a total concentration of the monomers, mol/L; t is a time, minute; 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. 4), corresponding to different values of the total concentration of monomers. Table 5 shows the copolymerization reaction rates calculated using equation (4) and other parameters. From the tabular data we can draw the following conclusion: with an increase in the total concentration of monomers by 3 times, the reaction rate increases by approximately 2 times.

This can be explained as follows: with increasing concentration of monomers, the probability of their collision (interaction) with active free radicals increases.

Table 5. Effect of the total concentration of monomers in the initial mixture on the yield of the TMAPMACh-IA copolymer. T = 343 K. $[(NH_4)_2S_2O_8]$ = 0.5 wt%. The molar composition of monomers in the mixture [TMAPMACh]:[IA] = 50: 50 mol.%.

[M], mol/L	1	1,5	2,0	3,0
$\frac{dy}{dt}$, min^{-1}	0,685	1,08	1,24	1,47
$R_c = [M]\frac{dy}{dt}$, mol/(l· min)	0,685	1,62	2,48	4,41
y(max), wt%	53	68	80	90
log R_c	-0,16	0,21	0,39	0,64
log [M]	0	0,18	0,30	0,48

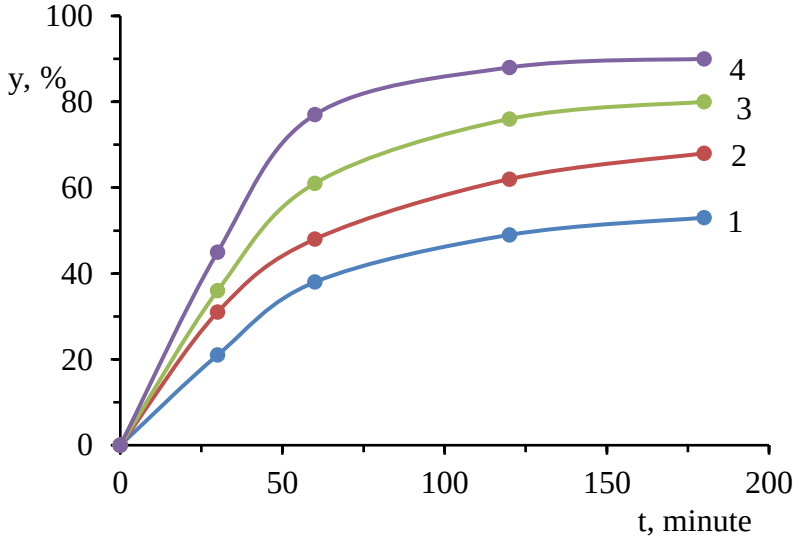


Fig. 4 Effect of the total concentration of monomers on the yield of the TMAPMACh-IA copolymer. Total concentration of monomers (mole/L): 1 (1); 1.5 (2); 2 (3) and 3 (4). $[(NH_4)_2S_2O_8]$=0.5 wt%. In a mixture of monomers [TMAPMACh]:[IA]=50:50 mol.%. T=343 K.

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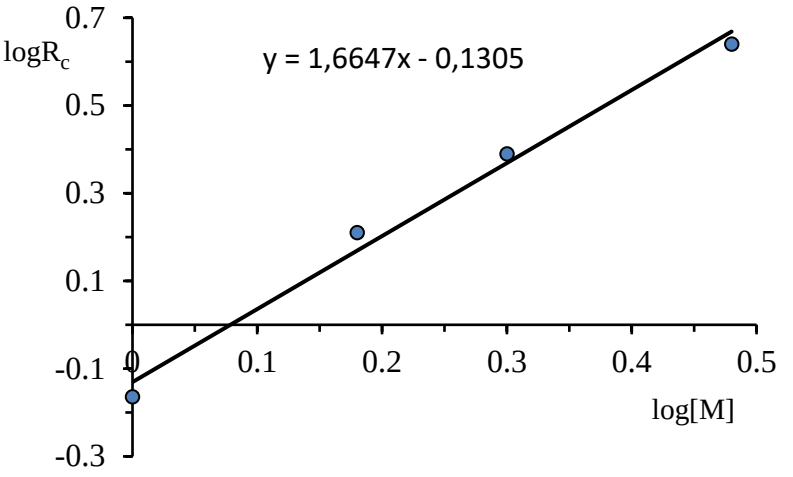


Fig. 5 Effect of the total concentration of monomers on the rate of the copolymerization reaction. [TMAPMACh]:[IA]=50:50 mol%. [$(NH_4)_2S_2O_8$] = 0.5 wt%. T=343 K.

Now you can plot the dependence log Rc = f(log[M]) and use it to determine the equation showing the dependence of the copolymerization reaction rate on the total concentration of monomers (Fig. 5). This equation looks like as follows: $R_c \propto [M]^{1,66}$.

In this work the effect of initiator concentration ($(NH_4)_2S_2O_8$) on the yield of the copolymer was also studied (Fig. 6). It was found that when the initiator concentration increased from 0.2 mol/L to 1.0 mol/L, the copolymer yield increased by 13% (Table 6).

The dependence of the copolymerization reaction rate on the initiator concentration was calculated using equation (5):

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

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

Table 6. Effect of the initiator concentration on the yield of the TMAPMACh-IA copolymer. T = 343 K. [M] = 2 mol/L. The molar composition of the monomers in the initial mixture is [TMAPMACh]:[IA] = 50: 50 mol.%. The initiator is $(NH_4)_2S_2O_8$.

[I], wt%	0,2	0,5	0,75	1,0
[I], mol/L	0,009	0,022	0,033	0,044
$\frac{dy}{dt}$, min^{-1}	1,04	1,22	1,54	1,86
$R_c = [M]\frac{dy}{dt}$, mole /(L· min)	2,08	2,44	3,08	3,72
y(max), wt%	75	80	85	92
log R_c	0,32	0,39	0,49	0,57
log [I]	-2,05	-1,66	-1,48	-1,36

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

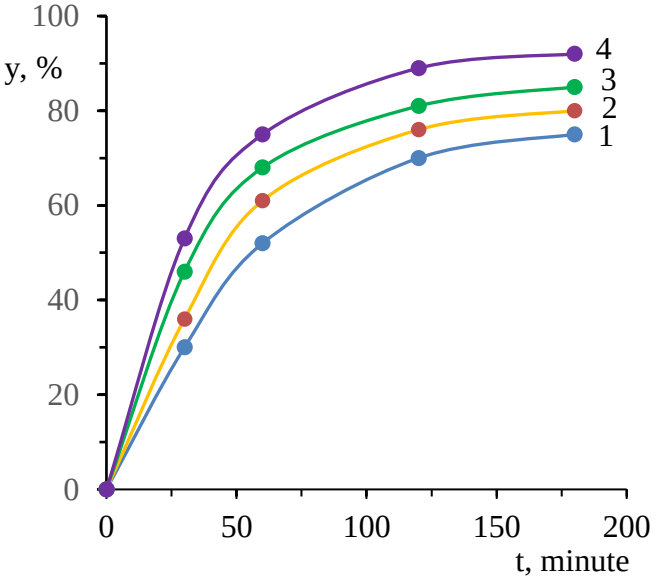


Fig. 6 Effect of initiator concentration on the yield of the TMAPMACh-IA copolymer. Initiator concentration (mol/L): 0.2 (1); 0.5 (2); 0.75 (3) and 1.0 (4). [M]=0.2 mol/L.%. In a mixture of monomers [TMAPMACh]:[IA] = 50:50 mol.%. T=343 K.

Now you can plot the dependence log R_c = f(log[I]) and use it to determine the equation showing the dependence of the copolymerization reaction rate on the initiator concentration (Fig. 7). This equation is written as follows: $R_c \propto [I]^{0,35}$.

Thus, the kinetic equation expressing the rate of the copolymerization reaction in the TMAPMACh-IA system (composition of the initial mixture [TMAPMACh]:[IA] = 50:50 mol%) at a temperature T = 343 K is written as follows:

$$R_c = k\times [M]^{1,66}\times[I]^{0,35}, \quad (6)$$

where k is the rate constant; [I] and [M] are the concentration

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of the initiator and the total concentration of monomers, respectively.

Then, using equation (6), we can calculate the rate constant (k) of the copolymerization reaction in the TMAPMACh-IA system.

1) From Table 5 under the condition [I] = 0.5 wt.% = 0.022 mol/L = const and at monomer concentration [M] = 2.0 mol/L, the copolymerization reaction rate is R_c = 2.48 mol/(L×min). Then equation (6) looks like as follows: 2.48 mol/(L×min)=k×[2.0 mol/L]$^{1.66}$×[0.022 mol/L]$^{0.35}$.

If we find the rate constant from last equation:

$$k = \frac{2{,}48}{([2{,}0]^{1{,}66}\times[0{,}022]^{0{,}35})} = \frac{2{,}48}{(3{,}16\times 0{,}26)} = 3{,}02\ \frac{L^{0,92}}{mol^{0,92}\times min} = 5{,}0\times 10^{-2}\ \frac{L^{0,92}}{mol^{0,92}\times s}.$$

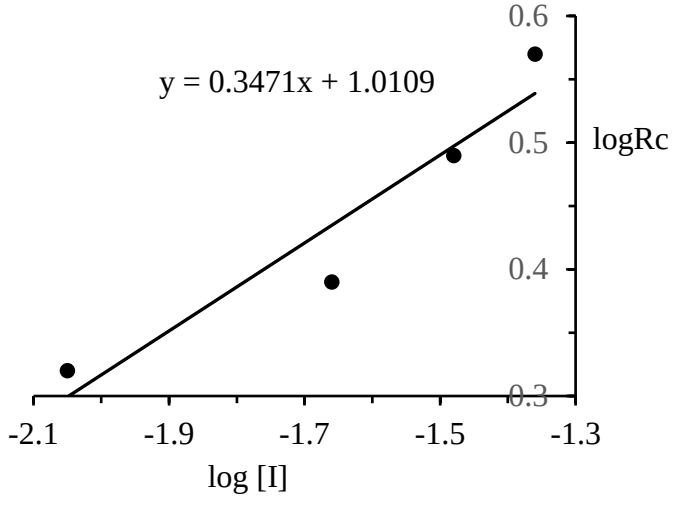


Fig. 7 Effect of the initiator concentration on the rate of copolymerization reaction. [TMAPMACh]:[IA]=50:50. [M] = 2 mol/L. T=343 K.

2) From Table 6 at [M]=2 mol/L =const and initiator concentration [I] = 0.5 wt% = 0.022 mol/L, the reaction rate is R_c = 2.44 mol/(L×min). Then equation (6) will look like as follows: 2.44 mol/(L×min)=k×[2 mol/L]$^{1.66}$×[0.022 mol/L]$^{0.35}$.

If we find the rate constant from last equation:

$$k = \frac{2{,}44}{([2]^{1{,}66}\times[0{,}022]^{0{,}35})} = \frac{2{,}44}{(3{,}16\times 0{,}26)} = 2{,}97\ \frac{L^{0,92}}{mol^{0,92}\times min} = 4{,}9\times 10^{-2}\ \frac{L^{0,92}}{mol^{0,92}\times s}.$$

Consequently, the average rate constant for the reaction of radical copolymerization in the TMAPMACh-IA system in the presence of $(NH_4)_2S_2O_8$ at a temperature T=343 K is equal to:

$$k_{av} = \frac{0{,}050 + 0{,}049}{2} = 4{,}95\times 10^{-2}\ \frac{L^{0,92}}{mol^{0,92}\times s}.$$

It has been noted in a number of works that the exponent of the total concentration of monomers in copolymerization reactions exceeds 1.0. For example, in article,[51] when analyzing the copolymerization reaction of N,N-diallyl-N,N-dimethylammonium chloride (DADMAC) with acrylamide (AA) at 45°C in the presence of a reducing complex of ammonium persulfate-sodium bisulfate, 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).

In the article,[52] during the studying the radical copolymerization reaction between DADMAC and vinyl ether of monoethanolamine (VEMEA) in the presence of an initiator $(NH_4)_2S_2O_8$ in a mixture with the composition [DADMAC]:[VEMEA] = 90:10 mol.% at 65°C, the following kinetic equation was obtained: $R_p = k\times[M]^{2.6}\times[I]^{0.6}$.

And in the article,[53] the radical copolymerization reaction of DADMAC with dimethylacrylamide (DMAA) in the presence of ammonium persulfate at 60°C was studied. The following kinetic equation was obtained: $R_p = k\times [M]^{2.63}\times [I]^{0.40}$.

In the work,[54] the copolymer DADMAC with N-[3-(dimethylamino)propyl]-methacrylamide (DADMAC-DMAPMA) was synthesized by radical copolymerization in an aqueous medium at 70°C in the presence of ammonium persulfate. For the DADMAC-DMAPMA system, the following kinetic equation was obtained: $R_c = k\times[M]^{3.48}\times[I]^{0.033}$.

3.3 Determination of the isoelectric point of a copolymer

In this work, the isoelectric point of the synthesized polyampholyte – the TMAPMAX-IA copolymer, was also determined. Fig. 8 shows the change in the reduced viscosity of an aqueous solution of the copolymer synthesized from the mixture [TMAPMACh]:[IA]=50:50 mol.%, depending on the pH value of the medium.

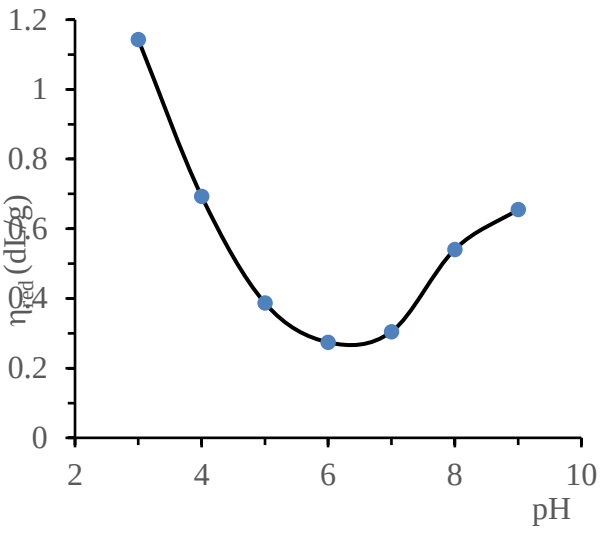
The figure shows that the isoelectric point of the copolymer corresponds to pH = 6.5. This result confirms that the TMAPMACh-IA copolymer is a polyampholyte.

At the isoelectric point, the polyampholyte has no charge; as a result, the polymer macromolecules have a compressed (approximately spherical) conformation and low viscosity. At pH < 6.5, macromolecules acquire a positive charge, and at pH > 6.5, macromolecules become negatively charged as a result of ionization of carboxyl groups of the copolymer TMAPMACh-IA. Due to the repulsion of similarly charged monomer units, the copolymer macromolecules acquire a more expanded conformation and the viscosity of the copolymer solution increases at 6.5 < pH < 6.5.

3.4 Study of the biocidal properties of TMAPMACh-IA copolymers

The biocidal properties of the synthesized copolymers against sulfate-reducing bacteria (SRB) were studied in the laboratory of environmental and agricultural microbiology of the

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T=298 K.

Fig. 8 Dependence of the reduced viscosity of an aqueous solutioncopolymer TMAPMACh-IA on the pH value of the environment.

Research and Production Center for Microbiology and Virology, Ltd (Almaty).

For the study, we selected copolymers synthesized from a mixture of monomers with the composition [TMAPMACh]:[IA] (mol%) = 40:60 (1), 50:50 (2) and 60:40 (3). The effect of these copolymer samples on the development of SRB was studied at five concentrations: 0.01%, 0.05%, 0.1%, 0.5% and 1.0%.

The biocidal properties of the copolymers against SRB bacteria were determined as follows: 1 mL of a culture of SRB bacteria was added to the test tubes and filled with Postgate medium, in which the required concentration of the copolymer was dissolved. To create anaerobic conditions, the tubes were closed with rubber stoppers. In the control variant (K), SRB was grown without the copolymer. Then the tubes were placed in a thermostat at 30°C for 15 days.

The study established that all studied samples of the TMAPMACh-IA copolymer completely (100%) inhibit the development of SRB bacteria within a concentration range of 0.5÷1.0 % (Figs. 9-11).

Copolymer sample (1) was found to be bactericidal against SRB starting at a concentration of 0.1%. The biocidal effect of the copolymer samples was observed throughout the entire testing period. At lower concentrations of copolymers (0.01÷0.05 %), no slowdown in the growth of SRB was observed.

On the inner surface of the tubes, the development of a black shell with a metallic sheen was observed (formation of iron sulfide), and the presence of bacterial cells was detected using a microscope. The smell of hydrogen sulfide was also observed.

Thus, we can conclude that the studied samples of the TMAPMACh-IA copolymer in the concentration range of 0.5÷1.0 % have a biocidal property, therefor they can be used to inhibit the growth of SRB bacteria. It should be also noted that the biocidal properties of the TMAPMACh-IA copolymer, synthesized from a mixture of monomers [TMAPMACh]:[IA] = 40:60 mol%, predominate. It completely inhibits the growth of SRB bacteria at a concentration of 0.1%.

As mentioned in the introduction, IA has antimicrobial, anti-inflammatory and antitumor activities. Therefore, an increase in the molar concentration of IA in the copolymer leads to an increase in the bactericidal properties of the latter. Nevertheless, the presence of a positive charge (quaternary ammonium group TMAPMACh) also contributes to the growth of the bactericidal properties of the copolymer, since the positively charged TMAPMACh group ensures ionic adsorption of copolymer macromolecules on the surface of negatively charged SRB.[44,45]

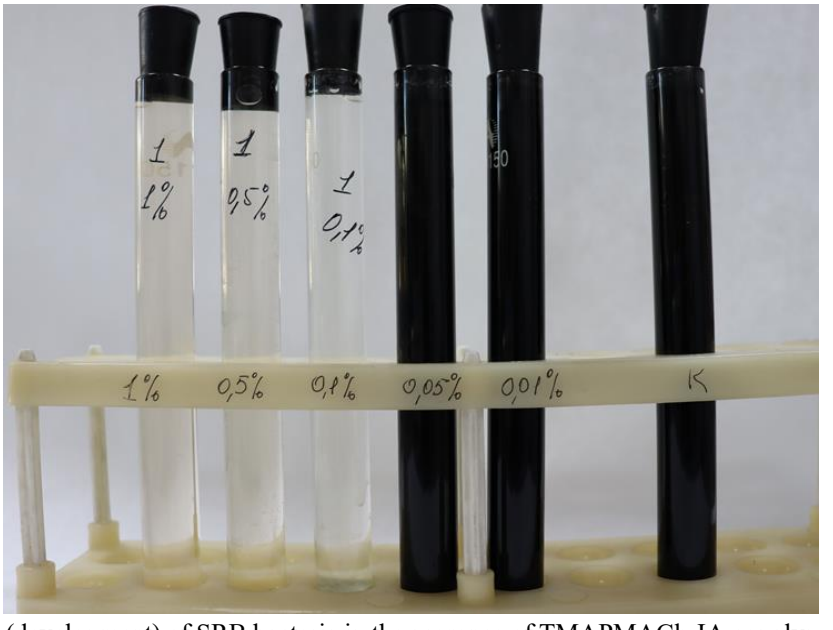


Fig. 9 Growth (development) of SRB bacteria in the presence of TMAPMACh-IA copolymer (40:60) (1).

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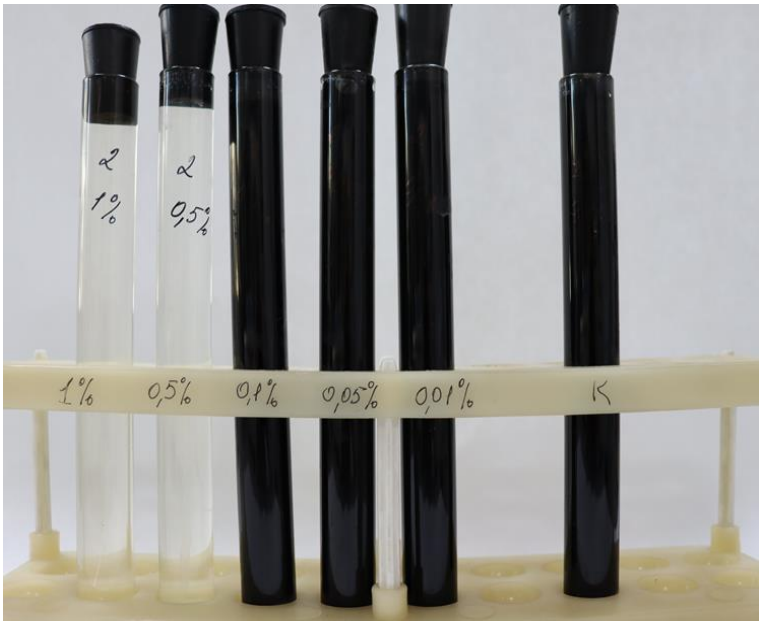


Fig. 10 Growth (development) of SRB bacteria in the presence of TMAPMACh-IA copolymer (50:50) (2).

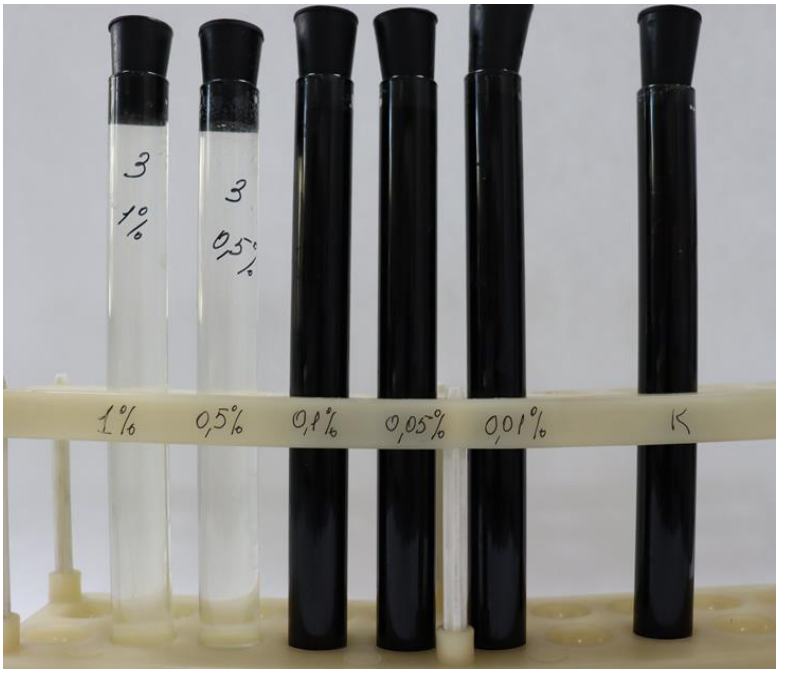


Fig. 11 Growth (development) of SRB bacteria in the presence of TMAPMACh-IA copolymer (60:40) (3).

4. Conclusions

1. A polyampholyte copolymer TMAPMACh-IA with different molar composition was synthesized 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, elemental analysis (for nitrogen) 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 TMAPMACh-IA copolymer increases. The kinetic equation for the TMAPMACh-IA system (composition of the initial mixture [TMAPMACh]:[IA]=50:50 mol%) at temperature T=343 K was written as follows: $R_c = k\times [M]^{1,66}\times[I]^{0,35}$.
4. The reactivity coefficients of monomers were calculated by using the Mayo-Lewis and Fineman-Ross equations. It was found that in the radical copolymerization reaction the IA monomer is more active than the TMAPMACh monomer. For this reason, the molar content of the IA monomer in the synthesized copolymer is always greater than that in the initial monomers' mixture.
5. The isoelectric point of the polyampholyte copolymer TMAPMACh-IA, synthesized from an equimolar mixture of monomers, was determined (pH_{isel} = 6.5).
6. The biocidal properties of the TMAPMACh-IA copolymer against SRB bacteria were determined. It has been established

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that TMAPMACh-IA copolymers in the concentration range of 0.5÷1.0 % have a biocidal effect. Therefore, they can be used to inhibit the growth of SRB.

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Conflict of Interest
There is no conflict of interest.

Supporting Information
Not applicable.

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