
MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Synthesis by Radical Polymerization and Structure of Drag Reducing Terpolymers Based on Acrylamide, Acrylonitrile, and 2-Acrylamido-2-methylpropanesulfonic Acid

A. I. Nechaev*, M. N. Gorbunova, I. I. Lebedeva, V. A. Val'tsifer, and V. N. Strel'nikov

Institute of Technical Chemistry, Ural Branch, Russian Academy of Sciences, ul. Akademika Koroleva 3, Perm, 614013 Russia

**e-mail: toxambj@gmail.com*

Received October 23, 2017

Abstract—Terpolymers of acrylamide, acrylonitrile, and sodium 2-acrylamido-2-methylpropanesulfonate were prepared by radical copolymerization in aqueous solution. The terpolymers obtained are enriched in acrylamide units and depleted of acrylonitrile units relative to the initial monomer ratio. The acrylamide–acrylonitrile–sodium 2-acrylamido-2-methylpropanesulfonic acid terpolymers show high performance as drag reduction agents. Under the conditions of thermal, salt, and acid aggressions, the terpolymer containing 71.6 mol % acrylamide, 10.5 mol % acrylonitrile, and 17.9 mol % sodium 2-acrylamido-2-methylpropanesulfonate ensures drag reduction no less than 70%.

DOI: 10.1134/S1070427217090233

One of applications of polymers in oil extraction is their use as components of drag reduction additives in aqueous and aqueous-organic media. This application is based on the Toms effect [1]. The extent to which polymer additives reduce the hydrodynamic resistance depends on the characteristics of the liquid flow, on the properties of the polymers, such as molecular mass, charge density, chain flexibility, structure, and morphology, and on the polymer concentration [2]. In particular, the extent to which the hydrodynamic resistance is reduced depends on the capability of polymers for intermolecular interactions and on the flexibility of their chain. These characteristics can be improved by increasing the molecular mass of the polymer and amount of ionic groups (charge density), and also by grafting smaller pendant groups to the polymer backbone.

High-molecular-mass flexible-chain linear copolymers based on acrylamide (AA) ensure the most pronounced drag reduction. In sinking deep and superdeep exploratory boreholes under complex geological conditions, when the drilling fluid should preserve its working characteristics at elevated temperatures ($\geq 90^\circ\text{C}$) and

high mineralization ($\geq 70\text{ g L}^{-1}$), polyacrylamide is of limited use [3].

AA copolymers with bulky sulfonate substituents in the pendant chain are more resistant to salt aggression at elevated temperatures [4]. Copolymerization of AA with various nonionic (e.g., acrylonitrile, AN [5]) and anionic (e.g., 2-acrylamido-2-methylpropanesulfonic acid, AMPSA, and its sodium salt, AMPSNa) monomers allows enhancement of the resistance to salts and heat, uniform distribution of ionic and nonionic substituents along the macromolecular chain, and an increase in the copolymer solubility. Also, as shown in [6], polyelectrolytes are characterized by larger solvation volume compared to nonionic polymers owing to electrostatic repulsion between the charged segments of the polymer chain, which, in turn, increases the extent to which these polymers reduce the hydrodynamic resistance to turbulent flow [7].

The majority of studies in the field of synthesis of acrylate copolymers deal with binary systems based on AA. For example, copolymerization of AA with AN [8], AMPSA [9], AMPSNa [10, 11], N-vinylpyrrolidone [12–14], styrene [15, 16], acrylic acid, vinylidene

chloride, methyl acrylate [17], and other monomers was studied. Papers on copolymerization of AA with two or more different monomers are relatively few. For example, synthesis of AA–AN–AMPSNa terpolymers containing up to 7.5 mol % AMPSNa and their sorption characteristics were described in [18–20]. The radical terpolymerization process and its parameters influencing the structure and, as a consequence, the antiturbulent properties were not studied in these works.

In the course of previous studies [21], we developed a procedure for preparing AA–AN–AMPSNa terpolymers with the monomer molar ratio in the reaction solution of (50–90) : (5–20) : (5–30). The terpolymers prepared at no less than 15 and 20 mol % content of AN and AMPSNa, respectively, in the initial monomer mixture appeared to be resistant to thermal and hydrothermal degradation up to 180°C, to CaCl₂ solutions of concentration up to 70 g L⁻¹, and to acids at pH down to 1.65. To reach the maximal reduction of the hydrodynamic resistance, it is necessary to prepare AA–AN–AMPSNa terpolymers with random distribution of ionic and nonionic units, which requires studying radical terpolymerization at preset monomer ratios.

In this study, we examined the specific features of radical terpolymerization of AA, AN, and AMPSNa and of copolymerization of each monomer pair in aqueous medium, obtained the diagrams of the composition of the co- and terpolymers, and determined the kinetic relationships of radical co- and terpolymerization. The extent to which the synthesized terpolymers reduce the hydrodynamic resistance to turbulent aqueous flows under the conditions of thermal, salt, and acid aggressions was studied.

EXPERIMENTAL

Acrylonitrile (99+%, Alfa Aesar) was purified by distillation; fraction with bp 78°C, n_D^{20} 1.3910, was used.

Acrylamide (98+%, Alfa Aesar), 2-acrylamido-2-methylpropanesulfonic acid (98%, Alfa Aesar), sodium hydroxide (analytically pure grade), and sodium sulfite (SS, analytically pure grade) were used without additional purification.

Potassium persulfate (PP, ≥99.0%, Sigma–Aldrich) used as polymerization initiator and the solvents after purification by standard procedures had the characteristics corresponding to the published data.

Terpolymerization of AA, AN, and AMPSNa was performed in water in the presence of PP, following

the previously developed procedure [21]. To an aqueous solution containing calculated amounts of AA and AMPSNa, we added a NaOH solution to pH 9 to maintain constant initiation rate at varied ionic strength of the solution. Then, the calculated amount of AN was added with stirring. The total concentration of the monomers in the solution was 1.6 M. The solution was bubbled with nitrogen through a finely porous glass frit for 15 min. Then, PP (polymerization initiator) and SS (oxygen scavenger), each at a concentration of 1×10^{-3} M, were added. The solution was placed in weighing bottles, which were tightly stoppered, placed in a thermostat, and kept there at 60°C. After the required degree of conversion was reached, the terpolymerization was stopped by cooling, and the products were precipitated with acetone. The terpolymers were washed three times with acetone and vacuum-dried at 50°C to constant weight.

The terpolymer composition was determined by elemental and thermal gravimetric analysis and was also calculated from the copolymerization constants of each monomer pair using the Alfrey–Goldfinger differential terpolymerization equation.

To determine the AA–AN, AN–AMPSNa, and AA–AMPSNa copolymerization constants, we studied how the composition of these copolymers depends on the composition of the initial monomer mixture under the same copolymerization conditions as for the ternary system. The copolymerization constants of the binary copolymer were calculated by the Fineman–Ross and Kelen–Tüdös methods.

Elemental analysis was performed with a Leco CHNS-9321P elemental analyzer (Netherlands). The sample weight was 2 mg, and the coefficient of variation was in the range 0.05–0.29%. The correction factors for sulfur and nitrogen were calculated from the results of elemental analysis of AMPSNa and AN homopolymers and were 0.5 and 1.5, respectively.

The ¹H and ¹³C NMR spectra were recorded with a Bruker Advance III HD 400 spectrometer (operating frequency 300 and 75.5 MHz, respectively). DMSO-*d*₆ was used as a solvent. The ¹³C NMR spectra were recorded with broadband proton decoupling and in the JMOD mode. The NMR spectra were taken using concentrated aqueous solutions of the polymers. The signals of groups in the terpolymer spectra were assigned on the basis of the reference data [22] taking into account the effect of the –SO₃ group.

The IR spectra were taken with a Bruker IFS 66/S spectrometer. Samples were prepared as KBr pellets (1 mg of the substance per 299 mg of KBr).

Thermal gravimetric analysis of the samples was performed with a TGA/DSC1 device (Mettler Toledo) in air at a heating rate of 10 deg min⁻¹ in the temperature interval 25–1000°C. The AMPSNa content was determined from the weight of the dry residue, Na₂SO₄, obtained upon heating the copolymer to 1000°C.

The kinetic relationships of the radical ter-polymerization in aqueous solution were studied by the dilatometric method and by differential scanning calorimetry (DSC). The DSC study was performed with a DSC822e device (Mettler Toledo) under oxygen-free conditions at heating rates of 2, 2.5, and 3 deg min⁻¹. The activation energy was determined by the isoconversion method using model-independent Friedman analysis [23].

The capability of the terpolymers to drag reduction *t* was evaluated with a capillary-type laboratory turbulent rheometer. The hydrodynamic performance of the terpolymers was evaluated by the relative decrease in the hydrodynamic resistance, *DR* (%), under the preset conditions of thermal, salt, and acid aggressions [1, 24]. The outflow time of a fixed volume of the pure solvent (water) and terpolymer solutions of different concentrations was measured with a capillary rheometer at the same pressure differential between the tube ends, $\Delta P_s = \Delta P_p = 8$ MPa. The quantity *DR* was calculated using the formula

$$DR = \left(1 - \frac{t_p^2}{t_s^2}\right) \times 100\%,$$

where *t_s* and *t_p* are the outflow times of a fixed volume of the pure solvent and polymer solution, respectively, through the capillary in the turbulent flow mode.

RESULTS AND DISCUSSION

AA–AN–AMPSNa terpolymers after precipitation with acetone were white powders soluble in water, DMSO, and DMF. It should be noted that AMPSA is neutralized in the process and is incorporated in the copolymer as the sodium salt.

According to the terminal unit model, three different types of terminal groups are formed in the course of copolymerization of three monomers M₁, M₂, and M₃: $\sim m_1$, $\sim m_2$, and $\sim m_3$. Each of them can react with any of the three monomers of the system; hence, there are nine different chain propagation reactions. The equations for the copolymer composition, derived by Alfrey and Goldfinger taking into account nine chain propagation reactions, allow quantitative prediction of the behavior of the ternary monomer system (M₁, M₂, and M₃) in copolymerization if the behavior of three monomer pairs (M₁–M₂, M₁–M₃, and M₂–M₃) in binary copolymerization is known:

$$\begin{aligned} d[M_1]:d[M_2]:d[M_3] &= [m_1]:[m_2]:[m_3] = [M_1] \left(\frac{[M_1]}{r_{31}r_{21}} + \frac{[M_2]}{r_{21}r_{32}} + \frac{[M_3]}{r_{31}r_{23}} \right) \left([M_1] + \frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}} \right) \\ &: [M_2] \left(\frac{[M_1]}{r_{12}r_{31}} + \frac{[M_2]}{r_{12}r_{32}} + \frac{[M_3]}{r_{32}r_{13}} \right) \left([M_2] + \frac{[M_1]}{r_{21}} + \frac{[M_3]}{r_{23}} \right) \\ &: [M_3] \left(\frac{[M_1]}{r_{13}r_{21}} + \frac{[M_2]}{r_{23}r_{12}} + \frac{[M_3]}{r_{13}r_{23}} \right) \left([M_3] + \frac{[M_1]}{r_{31}} + \frac{[M_3]}{r_{32}} \right), \end{aligned}$$

where [M₁], [M₂], and [M₃] are the monomer concentrations in the starting mixture (mol %); [m₁], [m₂], and [m₃] are the contents of the M₁, M₂, and M₃ monomer units in the copolymer (mol %); $r_{12} = k_{11}/k_{12}$, $r_{21} = k_{22}/k_{21}$, $r_{13} = k_{11}/k_{13}$, $r_{31} = k_{33}/k_{31}$, $r_{23} = k_{22}/k_{23}$, and $r_{32} = k_{33}/k_{32}$ are the copolymerization constants, or relative activities of the monomers.

Published data on the copolymerization constants of all the three monomer pairs for the conditions of our experiments are lacking. Therefore, we studied the dependences of the copolymer composition on

the composition of the initial monomer mixture for the binary systems AA–AN (M₁–M₂), AN–AMPSNa (M₂–M₃), and AA–AMPSNa (M₁–M₃) under these conditions.

The dependences of the compositions of the AA–AN, AN–AMPSNa, and AA–AMPSNa copolymers on the composition of the initial monomer mixture in copolymerization in aqueous solution, performed to low conversions (<10%), are shown in Fig. 1. The copolymers obtained were characterized by random distribution of units in the chain.

The effective copolymerization constants of AA (M_1) with AN (M_2) are $r_{12} = 1.188$ and $r_{21} = 0.057$. As can be seen, in copolymerization of AA with AN in aqueous solution in the presence of PP, AN is less active. Therefore, at all the compositions of the initial monomer mixture the copolymers are enriched in AA units.

In the plot of the composition of AN (M_2)–AMPSNa (M_3) copolymer vs. composition of the initial monomer mixture, there is an azeotropic point at the initial AMPSNa content of approximately 50 mol %, where the copolymer composition is equal to the composition of the monomer mixture. The effective copolymerization constants of AN (M_2) with AMPSNa (M_3) are $r_{23} = 0.193$ and $r_{32} = 0.162$. In this system, the reaction between different dissimilar radicals and monomers occurs under the conditions of our experiment more readily than the reaction between the similar radicals and monomers. Also, it is known that AN tends to heteropolymerization to a greater extent than to homopolymerization.

The effective copolymerization constants of AA (M_1) with AMPSNa (M_3) are $r_{13} = 1.05$ and $r_{31} = 0.5$. These values are similar to those obtained in copolymerization of AA with AMPSNa in aqueous solution in the presence of PP at $T = 30^\circ\text{C}$ ($r_{13} = 1.0$, $r_{31} = 0.52$).

The compositions of the AA–AN–AMPSNa terpolymer were calculated from the experimentally obtained AA–AN, AN–AMPSNa, and AA–AMPSNa copolymers using the Alfrey–Goldfinger equation. The calculation results are given in the table. The copolymer compositions found by elemental and thermal gravimetric analysis of the terpolymers are given for comparison.

As seen from the table, the calculated copolymer compositions agree on the whole with those determined by elemental and thermal gravimetric analysis, with somewhat underestimated calculated content of AMPSNa units and somewhat overestimated calculated content of AN units. At 65 mol % content of AA in the initial monomer mixture, irrespective of the AN : AMPSNa ratio, the terpolymers are enriched in AA units. At up to 60 mol % content of AA in the initial monomer mixture, the terpolymer is enriched in AN units relative to their content in the initial monomer mixture (15 mol %), and at >60 mol % AA content the terpolymer is depleted of these units. The content of AMPSNa units in the terpolymer is close to the content of AMPSNa in the initial monomer mixture.

As we showed previously, the terpolymer with the content of AA, AN, and AMPSNa units equal to 71.6,

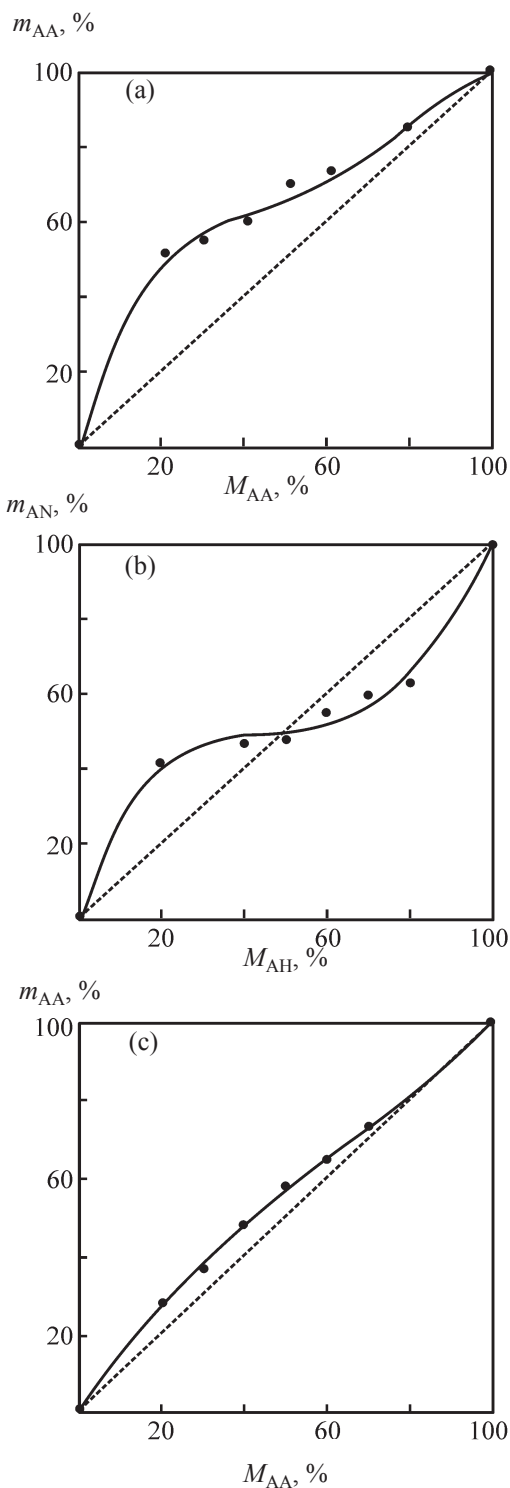


Fig. 1. Composition of the binary copolymers as a function of the composition of the initial monomer mixture. (a) AA–AN, (b) AN–AMPSNa, and (c) AA–AMPSNa. $[\Sigma M] = 1.6 \text{ M}$, $[\text{PP}] = 1 \text{ mM}$, $[\text{SS}] = 1 \text{ mM}$, $T = 60^\circ\text{C}$.

Composition of AA–AN–AMPSNa terpolymers (water, 60°C, $[M_1 + M_2 + M_3] = 1.6 \text{ M}$, $[\text{PP}] = 1 \text{ mM}$, $[\text{SS}] = 1 \text{ mM}$)

Composition of initial monomer mixture, mol %			Elemental analysis of copolymer, ^a wt %		Copolymer composition, ^a wt %						
					experimental data				calculated data		
					elemental analysis			TG			
AA	AN	AMPSA	N	S	AA	AN	AMPSNa	AMPSNa	AA	AN	AMPSNa
50	20	30	15.9	10.0	51.1	21.5	27.4	27.8	56	21	23
55	20	25	16.4	9.0	58.0	18.0	24.0	27.5	61	20	19
55	15	30	16.3	9.3	53.8	21.1	25.1	28.7	60	17	23
60	15	25	16.3	8.6	64.2	12.7	23.1	27.4	64	16	20
65	20	15	17.8	6.3	70.4	14.1	15.5	17.0	70	18	12
65	15	20	17.1	7.0	71.6	10.5	17.9	20.5	69	15	16
65	10	25	16.6	7.7	71.3	8.4	20.3	23.6	69	11	20
70	15	15	17.9	5.7	75.3	10.7	14.0	16.5	73	14	13
70	10	20	17.3	6.4	76.1	7.7	16.2	20.5	72	11	17
75	20	5	19.3	2.6	83.8	10.3	5.9	6.9	80	16	4
75	15	10	18.3	4.2	83.3	6.7	10.0	14.1	79	13	8
75	10	15	17.6	5.5	81.0	5.4	13.6	16.7	77	10	13
80	15	5	18.9	2.7	88.8	4.8	6.4	7.2	84	11	5
80	5	15	17.4	5.3	84.4	2.1	13.5	15.8	81	6	13

^a Taking into account the correction factor.

10.5, and 17.9 mol %, respectively ($[\text{AA}] : [\text{AN}] : [\text{AMPSNa}] = 65 : 15 : 20$), exhibits the minimum necessary level of heat, acid, and salt resistance at maximally aggressive operation conditions [21]. Therefore, we chose this terpolymer sample for further studies.

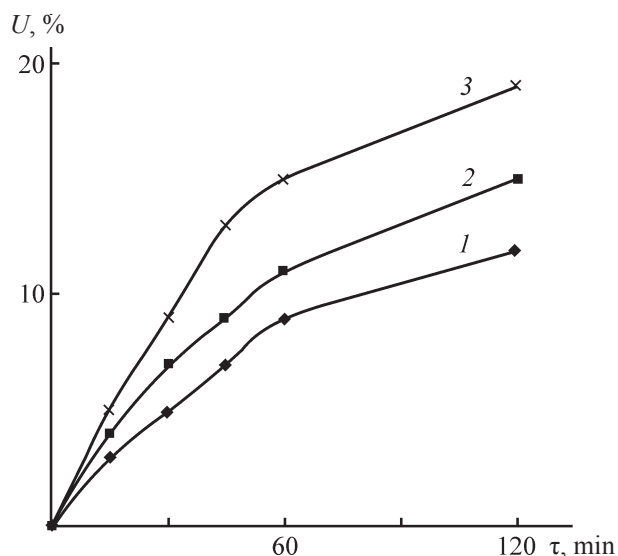


Fig. 2. Kinetic curves of (1) AMPSNa homopolymerization, (2) AMPSNa–AA copolymerization ($[\text{AMPSNa}] : [\text{AA}] = 20 : 80$), and (3) AMPSNa–AA–AN terpolymerization ($[\text{AA}] : [\text{AN}] : [\text{AMPSNa}] = 65 : 15 : 20$). $[\text{AA} + \text{AN} + \text{AMPSNa}] = 1.6 \text{ M}$, $[\text{PP}] = 1 \text{ mM}$, $[\text{SS}] = 1 \text{ mM}$, $T = 60^\circ\text{C}$. (U) Conversion and (τ) time.

A study of the copolymerization of AMPSNa with AA has shown that, in contrast to AMPSNa homopolymerization (Fig. 2, curve 1), the addition of AA (>50 mol %) leads to an increase in the overall process rate (Fig. 2, curve 2). An increase in the AMPSNa–AA copolymerization rate in an aqueous solution can be attributed to the formation of hydrogen bonds between the amide group of AA and water, leading to the redistribution of the electron density in the radical and thus to localization of the unpaired electron and appearance of partial positive charge on the nitrogen atom. As a result, the macroradical reactivity is enhanced, which is manifested in high rate constants of chain propagation. In addition, high reactivity of AA in aqueous solution can be attributed to the fact that hydrogen bonding with water molecules suppresses the self-association of the molecules of this monomer. Introduction of a small amount of AN (up to 15 mol %) leads to a further increase in the reaction rate (Fig. 2, curve 3), which may be due to a change in the macromolecule conformation on introducing more hydrophobic AN units, leading to a decrease in the termination constant.

A kinetic study has shown that the reaction orders with respect to the initiator and sum of the monomers (at the $[\text{AA}] : [\text{AN}] : [\text{AMPSNa}]$ ratio of 65 : 15 : 20) are 0.65 and 1.55, respectively, exceeding the values typical of radical polymerization. Increased reaction order with

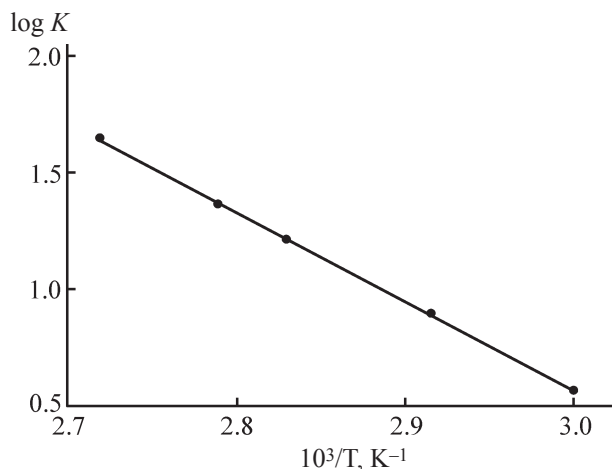


Fig. 3. Terpolymerization rate constant K as a function of temperature T in the Arrhenius coordinates for the system [AA] : [AN] : [AMPSNa] = 65 : 15 : 20. [AA + AN + AMPSNa] = 1.6 M, [PP] = 1 mM, [SS] = 1 mM.

respect to the monomer (1.5) was also observed in AMP-SA homopolymerization in water. This can be attributed to the occurrence of inter- and intramolecular interactions in the reaction system between the molecules of the monomers and water. In addition, significant contribution to the process kinetics is made by high viscosity of the reaction mixture already at low conversions.

The AA-AN-AMPSNa terpolymerization rate in the examined temperature interval (60–95°C) increases with temperature. The overall activation energy of the terpolymerization under the conditions of our

experiments, determined graphically using the Arrhenius equation (Fig. 3), is 73.22 kJ mol⁻¹ and is in the range characteristic of radical polymerization.

The structure of the terpolymers was studied by ¹H and ¹³C NMR spectroscopy. The NMR spectra were taken from concentrated aqueous solutions of the terpolymers. The signals of groups in the terpolymer spectra were assigned on the basis of reference data [22] taking into account the effect of the -SO₃ group.

The ¹H NMR spectrum of the terpolymer prepared at the initial monomer ratio AA : AN : AMPSNa = 65 : 15 : 20 (71.6 mol % AA, 10.5 mol % AN, 17.9 mol % AMPSNa) is shown in Fig. 4. In the ¹H NMR spectrum of the AA-AN-AMPSNa terpolymer, the chemical shifts of the signals from methylene protons in the backbone are observed at $\delta = 1.41$ –1.6 ppm. The signals observed at $\delta = 1.1$ –1.3 ppm correspond to protons of the CH₃ groups of AMPSNa. There are also signals at $\delta = 2.08$ ppm, corresponding to -CH₂-CH protons of AA and AMPSNa units of the polymer chain. The signals at $\delta = 2.61$ –2.9 ppm correspond to -CH₂-CH protons of AN units. The signal at $\delta = 3.34$ ppm belongs to methylene protons of the C-CH₂-S fragment, and the broad signal at $\delta = 3.41$ ppm corresponds to water protons. The signals of NH₂ protons of AA units and NH protons of AMPSNa units are observed at δ 6.69–7.15 and 7.49–8.39 ppm, respectively.

The ¹³C NMR spectrum of the terpolymer (71.6 mol % AA, 10.5 mol % AN, 17.9 mol % AMPSNa) is shown

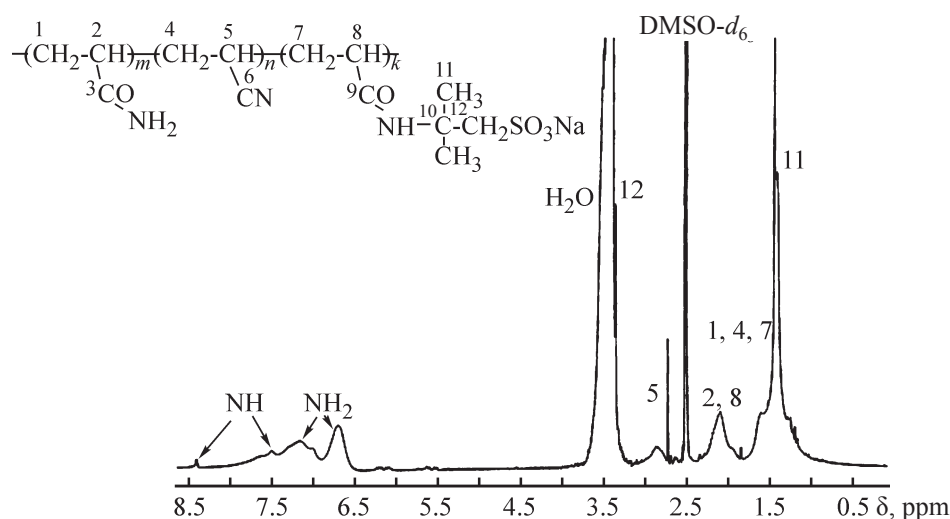


Fig. 4. ¹H NMR spectrum of the AA-AN-AMPSNa terpolymer (71.6 mol % AA, 10.5 mol % AN, 17.9 mol % AMPSNa), DMSO-*d*₆. (δ) Chemical shift; the same for Fig. 5.

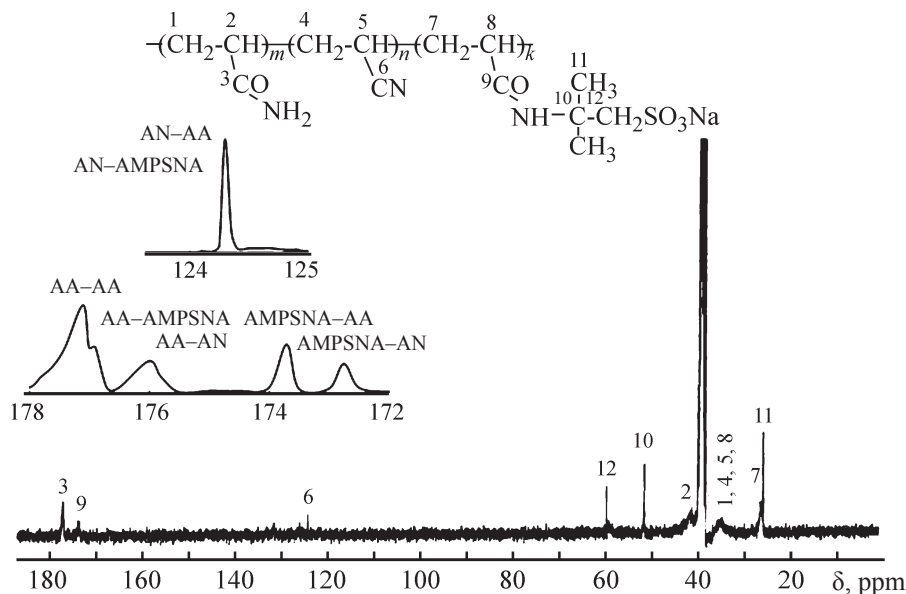


Fig. 5. ^{13}C NMR spectrum of the AA-AN-AMPSNa terpolymer (71.6 mol % AA, 10.5 mol % AN, 17.9 mol % AMPSNa), $\text{DMSO-}d_6$.

in Fig. 5. The signals at 171–177 ppm correspond to carbonyl carbon atoms, and the signal at 123 ppm, to the nitrile carbon atom. There are also signals from the C^{10} quaternary carbon atom at 51.70 ppm and from the C^{12} carbon atom of the methylene group bonded to the SO_3 group in the AMPSNa unit at 60.11 ppm. The signal at 25.73 ppm in the spectra corresponds to the C^{11} carbon atoms of two methyl groups. More detailed analysis of the ^{13}C NMR signals of the carbonyl and nitrile groups reveals the presence of AA-AA, AA-AMPSNa, AA-

AN, AMPSNa-AA, AMPSNa-AN, AN-AA, and AN-AMPSNa compensation diads in the AA-AN-AMPSNa terpolymer (71.6 mol % AA, 10.5 mol % AN, 17.9 mol % AMPSNa). The terpolymers are characterized by the presence of AA-AA blocks because of high AA content. AMPSNa-AMPSNa and AN-AN diads are not observed in the ^{13}C NMR spectrum of the terpolymer; hence, blocks of sulfonic acid and acrylonitrile units are not formed in the terpolymers.

The concentration dependences of the extent to which the AA-AN-AMPSNa terpolymer (71.6 mol % AA, 10.5 mol % AN, 17.9 mol % AMPSNa) reduces the hydrodynamic resistance under normal conditions and under the conditions of thermal, salt, and acid aggressions are shown in Fig. 6.

Our experiments show that the AA-AN-AMPSNa terpolymer (71.6 mol % AA, 10.5 mol % AN, 17.9 mol % AMPSNa) decreases the hydrodynamic resistance by no less than 70% compared to the untreated water at terpolymer concentrations higher than 0.1 wt %. The profile of the concentration dependence and the extent to which the hydrodynamic resistance decreases, DR, remain unchanged in CaCl_2 solutions with concentrations of up to 70 g L^{-1} (7 wt %). Efficient reduction of the hydrodynamic resistance by the AA-AN-AMPSNa terpolymer (71.6 mol % AA, 10.5 mol % AN, 17.9 mol % AMPSNa) in a salt solution is due to introduction of AMPSA, which contains sulfonate anion

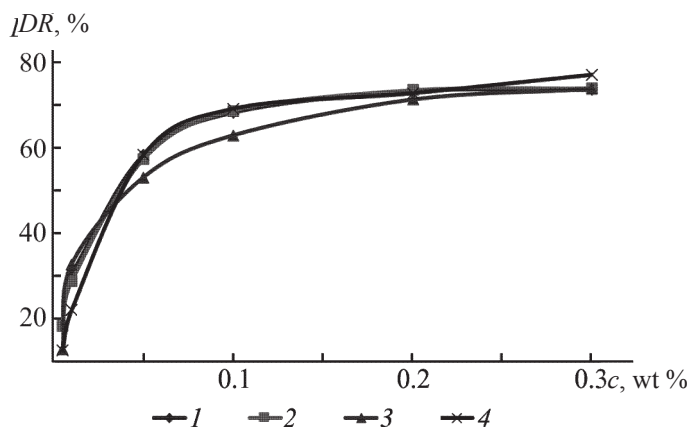


Fig. 6. Extent DR to which the terpolymer (71.6 mol % AA, 10.5 mol % AN, 17.9 mol % AMPSNa) decreases the hydrodynamic resistance to the flow of (1) distilled water at 25°C , (2) 70 g L^{-1} CaCl_2 solution at 25°C , (3) buffer solution with pH 1.65 at 25°C , and (4) distilled water at 140°C as a function of the terpolymer concentration c .

and is a strong acid that does not form poorly soluble salts with the bivalent calcium cation. As pH of the medium is decreased to 1.65, DR for the terpolymer in its dilute solutions slightly decreases (by 3–5%), with the character and profile of the concentration dependence remaining the same. This decrease may be due to suppression of the dissociation of the carboxy groups in the copolymer with decreasing pH and, as a consequence, to a decrease in the size of polymer coils. On the other hand, a decrease in pH to 1.65 does not lead to a decrease in the maximal value of DR (71%). The hydrodynamic resistance at elevated temperatures (up to 140°C) is efficiently decreased at terpolymer concentrations higher than 0.12 wt %.

CONCLUSIONS

Acrylamide enters into radical copolymerization with acrylonitrile and 2-acrylamido-2-methylpropanesulfonic acid to form random terpolymers with uniform distribution of ionic (sodium 2-acrylamido-2-methylpropanesulfonate) and nonionic (acrylonitrile) units along the macromolecular chain, which ensures high performance of the acrylamide–acrylonitrile–sodium 2-acrylamido-2-methylpropanesulfonate terpolymer as an additive reducing the hydrodynamic resistance to aqueous flow.

Experiments on the reduction of hydrodynamic resistance to aqueous flows, performed with solutions containing up to 70 g L⁻¹ CaCl₂, with acidified solutions (pH down to 1.65), and at elevated temperatures (up to 140°C), show that introduction of the terpolymer containing 71.6 mol % acrylamide units, 10.5 mol % acrylonitrile units, and 17.9 mol % sodium 2-acrylamido-2-methylpropanesulfonate units with random distribution of ionic and nonionic units at optimum terpolymer concentrations (0.1–0.2 wt %) ensures efficient reduction of the hydrodynamic resistance (DR_{\max} is in the range 70–75%).

ACKNOWLEDGMENTS

The study was financially supported by the Ministry of Education and Science of the Russian Federation (agreement no. 14.607.21.0121, project identifier RFMEFI60715X0121).

REFERENCES

1. Abubakar, A., Al-Wahaibi, T., Al-Wahaibi, Y., et al., *Chem. Eng. Res. Des.*, 2014, vol. 92, pp. 2153–2181.
2. Abubakar, A., Al-Hashmi, A.R., Al-Wahaibi, T., et al., *Adv. Mech. Eng.*, 2014, vol. 6, pp. 1–8.
3. Ma, Q., Shuler, P.J., Aften, C.W., and Tang, Y., *Polym. Degrad. Stab.*, 2015, vol. 121, pp. 69–77.
4. Kelland, M.A., *Production Chemicals for the Oil and Gas Industry*, Boca Raton: CRC, 2014, 2nd ed.
5. Orlyanskii, V.M., Novakov, I.A., and Navrotskii, A.V., *Tekhnol. Polim.*, 2009, no. 8, pp. 11–15.
6. Limparyoon, N., Seetapan, N., and Kiatkamjornwong, S., *Polym. Degrad. Stab.*, 2011, vol. 96, pp. 1054–1063.
7. Le Brun, N., Zadrazil, I., Norman, L., et al., *Chem. Eng. Sci.*, 2016, vol. 146, pp. 135–143.
8. Chen Hou, Liang Ying, and Chengguo Wang, *J. Mater. Sci.*, 2005, vol. 40, pp. 609–612.
9. Travas-Sejdic, J. and Easteal, A., *J. Appl. Polym. Sci.*, 2000, vol. 75, no. 5, pp. 619–628.
10. Kurenkov, V.F., Kurenkov, A.V., and Lobanov, F.I., *Polym. Sci., Ser. B*, 2011, vol. 53, no. 3, pp. 132–136.
11. Sun, Q., Zhang, C., Gao, Y., et al., *J. Funct. Mater.*, 2012, vol. 9, pp. 1151–1157.
12. Yetimoğlu, E.K., Kahraman, M.V., Ercan, Ö., et al., *React. Funct. Polym.*, 2007, vol. 67, pp. 451–460.
13. An, Y., Jiang, G., Qi, Y., et al., *J. Petrol. Sci. Eng.*, 2015, vol. 135, pp. 505–514.
14. Xu, L., Che, L., Zheng, J., et al., *RSC Adv.*, 2014, vol. 4, no. 63, pp. 33269–33278.
15. Oketola, A.A. and Torto, N., *Adv. Nanopart.*, 2013, vol. 2, pp. 87–93.
16. Ge, Z. and Luo, Y., *J. Appl. Polym. Sci.*, 2009, vol. 114, no. 3, pp. 1457–1463.
17. Mohan, Y.M., Murthy, P.S.K., and Raju, K.M., *React. Funct. Polym.*, 2005, vol. 63, no. 1, pp. 11–26.
18. Kazantsev, O.A., Shirshin, K.V., Sivokhin, A.P., et al., *J. Polym. Res.*, 2012, vol. 19, no. 6, p. 9886.
19. Budanova, Y.E., Shvetsov, O.K., and Maer, Z.A., *Russ. J. Appl. Chem.*, 2001, vol. 74, no. 7, pp. 1215–1219.
20. Ma, J., Zheng, H., Tan, M., et al., *J. Appl. Polym. Sci.*, 2013, vol. 129, no. 4, pp. 1984–1991.
21. Nechaev, A.I., Lebedeva, I.I., Val'tsifer, V.A., and Strel'nikov, V.N., *Russ. J. Appl. Chem.*, 2016, vol. 89, no. 8, pp. 1296–1301.
22. Badertscher, M., Bühlmann, P., and Pretsch, E., *Structure Determination of Organic Compounds*, Berlin: Springer, 2009.
23. Vyazovkin, S., Burnhamb, A.K., Criadoc, J.M., et al., *Thermochim. Acta*, 2011, vol. 520, pp. 1–19.
24. Kamel, A. and Shah, S.N., *J. Petrol. Sci. Eng.*, 2009, vol. 67, pp. 23–33.