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COPOLYMERS OF SODIUM 2-ACRYLAMIDO-2-METHYLPROPANESULFONATE FOR THE PRODUCTION OF GEL-FORMING COMPOSITIONS

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Abstract

Copolymers of sodium 2-acrylamido-2-methylpropanesulfonate with acrylamide, methacrylamide, sodium acrylate and sodium methacrylate have been synthesized. The influence of the chemical structure of acrylic and methacrylic acid derivatives on the copolymer's unit ratio, chain length, interaction with polyvalent metal salts, formation of polyelectrolyte hydrogels and thermo-oxidative stability of copolymers has been established. The molar ratios of units in copolymers were determined based on the composition of the initial monomer mixture. The relative activities of monomers in the copolymerization reaction of sodium 2-acrylamido-2-methylpropanesulfonate with methacrylic acid derivatives were calculated. Copolymerization of sodium 2-acrylamido-2-methylpropanesulfonate with acrylamide, methacrylamide and sodium acrylate leads to depletion, and with sodium methacrylate – to enrichment of the copolymers with sodium 2-acrylamido-2-methylpropanesulfonate units. The chain links are statistically distributed in all copolymers. The longest chains are formed as a result of copolymerization with acrylamide, while the shortest chains are obtained with methacrylamide. The formation of polyelectrolyte hydrogels from salts of polyvalent metals is achieved by the interaction of copolymer solutions with chromium and aluminum triacetate. It has been shown that, along with sulfonated polyacrylamide, copolymers of sodium 2-acrylamido-2-methylpropanesulfonate with sodium methacrylate have the potential to be used in high-temperature oil reservoirs in the oil-producing industry. The thermal-oxidative stability of the copolymer does not lead to its decomposition at reservoir temperature

Keywords: *copolymer, sodium 2-acrylamido-2-methylpropanesulfonate, acrylamide, methacrylamide, sodium acrylate, sodium methacrylate, polyelectrolyte hydrogel*

Introduction

Aqueous solutions of the copolymer (CP) of sodium 2-acrylamido-2-methylpropanesulfonate (AMPSNa) and acrylamide (AAm), known as sulfonated polyacrylamide, commonly have been found application in the oil industry in technologies for limiting water inflows in oil reservoirs [1, 2]. The interaction of polymer solutions with salts of polyvalent metals (Cr^{3+}, Al^{3+}, Zr^{4+}, etc.) under the influence of elevated oil reservoir temperatures produces coordination-crosslinked polyelectrolyte hydrogels (PEGG) [3].

Gelling compositions are exposed to long-term reservoir temperatures, which leads to the deterioration of their properties due to the destruction and changes in the chemical structure of the polymer, mainly due to acrylamide links. To improve thermal stability, it is recommended to replace the acrylamide units in AMPSNa CP with units of other derivatives of acrylic and methacrylic acids. Copolymers of AMPSNa with AAm and methacrylamide (MAAm), sodium acrylate and sodium methacrylate (ANa, MANa) were synthesized.

The incorporation of methacrylic acid derivatives, such as sodium methacrylate, enhances the thermal and chemical stability of polymeric gels, improving their performance in high-temperature reservoirs [4, 5]. Copolymer interactions with metal salts like chromium and aluminum play a key role in forming stable, oxidation-resistant gels [9, 10]. The coordination crosslinking with Cr (III) and Al (III) results in stronger, more durable gels suitable for harsh reservoir conditions [6].

This study examines how the second monomer unit in AMPSNa copolymers influences composition, chain length, metal salt interactions, PEGG formation, and thermal-oxidative stability. Understanding these factors will help develop more efficient and durable gel-forming compositions for oilfield applications [7, 8].

The aim of this work is to establish the influence of the chemical structure of the units of the second monomer in the AMPSNa CP on the ratio of units, the length of the CP chain, the interaction with polyvalent metal salts, the formation of PEGG and the thermal-oxidative stability of the copolymers.

Experimental Part

The polymers were obtained through free-radical polymerization in an aqueous solution. In the synthesis, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) with a main substance content of 98.0% (Alfa Aesar, USA) with a melting point of 185 ºC was used without preliminary purification. Acrylic and methacrylic acids were purified by distillation under reduced pressure. AAm was recrystallized from chloroform, and MAAm was recrystallized from ethyl acetate. To neutralize AMPS and other monomeric acids, analytical-grade sodium hydroxide and distilled water were used, without further purification. The polymerization was initiated by a redox system consisting of ammonium persulfate $(NH_4)_2S_2O_8$ and sodium sulfite Na_2SO_3 from Gomel Chemical Plant, Belarus. To isolate homo- and copolymers from the aqueous solutions, analytical-grade acetone was used as a precipitant.

Depending on the composition of the monomer mixture, a calculated amount of AMPS was placed in a three-necked flask equipped with a stirrer, thermometer, reflux condenser and cooled in an ice-water bath, and dissolved in distilled water. To neutralize the solution during cooling, a solution of the calculated amount of NaOH was gradually added using a water bath. Once the pH reached 7, the second monomer was added to the solution. After it dissolved, mixed solutions of initiators with a concentration of 10% by weight were introduced. The temperature of the reaction mixture was increased to 71–72 ºC. The reaction continued for 4 h, then cooled to room temperature. After completion of the synthesis, the polymer was purified by precipitation from the aqueous solution into acetone and dried at 50 ºC. Homopolymers were synthesized using the same method without addition of the second monomer.

The composition of the copolymers was determined by IR spectroscopy using a Bruker Alpha spectrometer with a Platinum-ATR attachment (Bruker, Germany). The relative activities of the monomers (copolymerization constants) were calculated using the Fineman-Ross and Kelen-Tudos equations [9, 10].

The length of the copolymer chains was estimated by viscometry by comparing the values of the intrinsic viscosity ([η]) of the copolymers with [η] and the molecular weight (M) of the homopolymers.

The resistance of the copolymers to thermal-oxidative degradation in air was assessed using a NETZSCHSTA 449 F3 Jupiter thermal analyzer (NETZSCH, Germany) in the temperature range of 20–500 ºC using a combined thermal analysis method, including thermogravimetry (TG), differential TG (DTG), and differential scanning calorimetry (DSC). The measurements were carried out at a heating rate of 10 ^{o}C/min in a corundum crucible.

Gelling compositions were obtained by dissolving powdered polymer in distilled water with the addition of a solution of a crosslinking agent - salts of Mn, Fe, Cu, Zn, as well as Mg, Cr and Al. Hermetically sealed solutions of the compositions in transparent containers were placed in a thermostat heated to a temperature of 95 ^{o}C. At certain intervals, samples were removed from the thermostat to assess their appearance and consistency, following the bottle test procedure described in [11]. The onset time of gelation was determined at the moment of transition of the composition consistency from the state of a viscous solution (code B) to the state of a very plastic, highly fluid gel (code C). The technologically acceptable time for the onset of gelation of the compositions at reservoir temperature should be no less than 4 hours and no more than 24 h. The polymer concentration in water was varied from 1 to 10% by weight, and the metal cation concentration was varied from 200 to 1600 mg/l.

Results and Discussion

Tab. 1 shows the dependences of the molar fraction of AMPSNa units in the copolymer (β) from the molar fraction of AMPSNa in the initial monomer mixture (α). It can be observed that during the copolymerization of AMPSNa with AAm, MAAm and ANa, depletion occurs, and with MANa, enrichment of the copolymers with AMPSNa units occurs.

The relative activities of monomers (copolymerization constants) in the radical copolymerization reaction of AMPSNa with MANa and MAAm in aqueous solutions, calculated by different methods, are very close. Therefore, Tab. 2 presents only the values determined by the Fineman-Ross method. The copolymerization constants of AMPSNa with acrylic acid derivatives were known previously [12, 13].

Table 1. Dependence of the mole fraction of AMPSNa units in the copolymer (β) from the mole fraction of AMPSNa in the monomer mixture (α)

Ratio of AMPSNa : comonomer in the synthesis of CP, mol :mol	Comonomer	3 : 7	1 : 1	7 : 3	8 : 2
α, mole fractions		0.3	0.5	0.7	0.8
β, mole fractions	AAm	0.23	0.38	0.61	0.72
	MAAm	0.20	0.32	0.45	0.58
	ANa	0.16	0.25	0.34	0.43
	MANa	0.39	0.53	0.73	0.80

Table 2. Relative activities of monomers (r_2) in the reaction of radical copolymerization with AMPSNa (r_1)

Monomer		Relative activity		Source
		r_1	r_2	
AMPSNa	AAm	0.11±0.01	1.31±0.09	[8]
same	MAAm	0.17±0.03	1.42±0.05	[5]
-«-	ANa	0.12±0.01	2.03±0.03	[7]
-«-	MANa	0.87±0.09	0.50±0.05	[4]

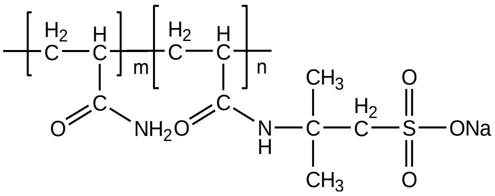
According to the data in Tab. 2, the product of the relative activity $r_1 \cdot r_2$ for all copolymers is less than one, which indicates a statistical distribution of links in the chain.

Tab. 3 presents the values of the intrinsic viscosity [η] and molecular weight M of homopolymers: sodium poly-2-acrylamido-2-methylpropanesulfonate (PAMPSNa), polyacrylamide (PAAm), sodium polyacrylate (PANa), polymethacrylamide (PMAAm) and the intrinsic viscosity of copolymers. Their comparison shows that the longest chain length is that of the CP AMPSNa and AAm, and the shortest is that of the CP AMPSNa and MAAm. Copolymers with sodium salts of acrylic and methacrylic acids have intermediate [η] values in the molecular weight range from $1 \cdot 10^6$ to $2 \cdot 10^6$ Da. The chain length of the copolymer of AMPSNa and MANa is higher than that of the copolymer of AMPSNa and ANa.

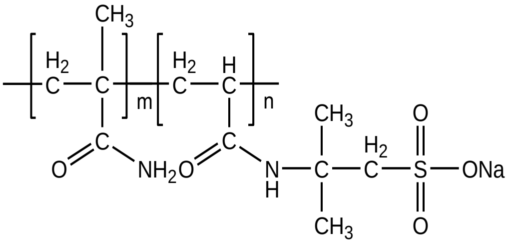
Table 3. Values of intrinsic viscosity and molecular weight of homopolymers and intrinsic viscosity of copolymers

Polymer	[η], dl/g	M, Da	Copolymer	[η], dl/g
PAMPSNa	2.03	$2.31 \cdot 10^6$		
PAAm	3.50	$3.85 \cdot 10^6$	AMPSNa and AAm	3.06
PMAAm	0.12	$2.7 \cdot 10^3$	AMPSNa and MAAm	0.41
PANa	1.95	$2.8 \cdot 10^5$	AMPSNa and ANa	1.47
PMANa	1.13	$(1\text{-}2) \cdot 10^6$	AMPSNa and MANa	1.72

Fig. 1 shows the chemical structure of copolymers of AMPSNa with AAm, MAAm, ANa and MANa.



AMPSNa and AAm CP



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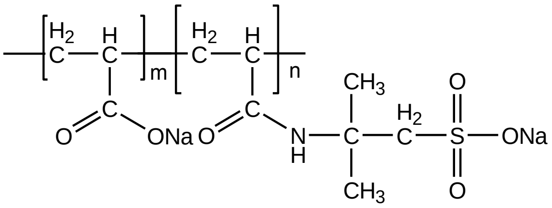
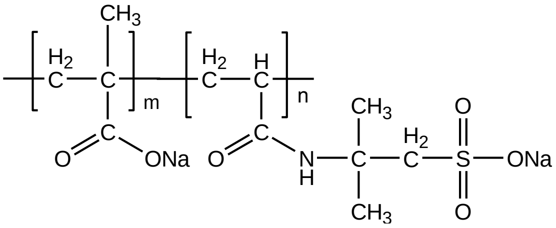


AMPSNa and ANa CP



AMPSNa and MANa CP

Fig. 1. Structural formulas of copolymers AMPSNa with AAm, MAAm, ANa and MANa

Gelling compositions based on aqueous solutions of the synthesized copolymers were obtained using the classical crosslinking agent chromium triacetate (Cr(III)acetate). Compositions containing PAMPSNa and Cr(III)acetate did not–exhibit gelling properties. Increasing the PAMPSNa concentration to 10% or raising the chromium ion concentration to 1600 mg/L did not result in gel formation. Heating of PANa-based compositions with different concentrations of Cr(III)acetate resulted in precipitation of chromium polyacrylate powder.

An assessment of the possibility of using AMPSNa and MAAm CP for the creation of gel-forming compositions showed that, due to the short chain length of PMAAm and CP MAAm with AMPSNa, it is necessary to use polymer solutions with a concentration higher than 10% by weight, regardless of the amount of Cr(III)acetate, which is economically impractical.

Despite the higher chain length of the AMPSNa and ANa copolymer, its required concentration in the gelling compositions also reached approximately 10% by weight. In addition, the copolymer is significantly enriched with ANa units. Due to the lack of interaction of Cr^{3+} cations with the sulfonate groups of AMPSNa units and the formation of complexes exclusively with carboxylate groups [14], the high number of ANa units in the CP led to an increase in the crosslinking density and a decrease in the water absorption of PEGG.

To reduce the concentration of carboxylate groups during the production of CP with AMPSNa, sodium acrylate was replaced with sodium methacrylic acid. As can be seen from the data in Tab. 1 and 2, the copolymer of AMPSNa and MANa is depleted in MANa units. The replacement of the comonomer led not only to a decrease in the concentration of carboxylate groups, but also made it possible to reduce the concentration of CP in the gelling composition to 2% by weight.

Tab. 4 presents the gelation dynamics of compositions containing Cr(III) acetate, based on 2% solutions of AMPSNa-MANa copolymer (CP) and PMANa in both distilled water and a groundwater model, maintained at 95 °C. The concentration of Cr^{3+} cations was 800 mg/l. The optimal number of MANa units in the copolymer with AMPSNa was determined to be 0.24-0.38 mole fractions. The presence of hardness salts in groundwater reduced the swelling capacity of PEGG by 3.5-9.6 times while maintaining nearly the same gel index. This effect is attributed to the suppression of polyelectrolyte swelling of the copolymer in the presence of low-molecular-weight electrolytes.

Based on the APMSNa and MANa CP, the possibility of using solutions of salts of other d-elements as cross-linking agents for creating gel-forming compositions was investigated: Mn, Fe, Cu, Zn, as well as Mg and Al. It was shown that as a result of the formation of an intramolecular complex, acetates and chlorides of divalent copper caused the formation of a precipitate of CP. Similarly, aluminum sulfate, iron citrate and iron oxalate also led to precipitate formation. When using salts of other divalent cations, gelation throughout the entire volume of the composition did not occur. Solutions of Al^{3+} and Fe^{3+} chlorides immediately formed non-flowing PEGG, while gelling compositions must remain fluid for 4 to 24 h to be properly delivered to the oil reservoir. It was established that in addition to Cr(III)acetate, PEGG with a copolymer of AMPSNa and MANa forms Al(III)acetate.

Changing the pH of the composition did not have a significant effect on the formation of PEGG. Hydrogels with Cr(III)acetate were stronger and less fluid compared to those with Al(III)acetate. They have a larger gel fraction, but a lower degree of swelling. Thus, Al(III)acetate, along with Cr(III)acetate, can be used as a crosslinking agent for aqueous solutions of AMPSNa and MANa CP. The crosslinking efficiency of aluminum acetate is lower than that of Cr(III)acetate, but PEGGs are able to retain more water.

Table 4. Dynamics of gelation of compositions based on 2% solutions of AMPSNa and MANa CP with Cr(III)acetate at a temperature of 95 ^{o}C

<table>
<tr><th colspan="9">Solution identical to ground water, pH=7</th></tr>
<tr><th rowspan="2">Mole fraction of MANa in a mixture of monomers</th><th rowspan="2">Mole fraction of MANa units in CP</th><th colspan="7">Heating time, h</th></tr>
<tr><th>0</th><th>4</th><th>6</th><th>10</th><th>15</th><th>20</th><th>24</th></tr>
<tr><td>0.2</td><td>0.15</td><td colspan="2" rowspan="5">B</td><td colspan="2">B/C</td><td colspan="3">C</td></tr>
<tr><td>0.3</td><td>0.24</td><td>B/C</td><td>C</td><td>C/D</td><td colspan="2">D</td></tr>
<tr><td>0.5</td><td>0.38</td><td rowspan="2">B</td><td>B/C</td><td>C</td><td colspan="2">C/D</td></tr>
<tr><td>0.7</td><td>0.59</td><td colspan="4">B/C</td></tr>
<tr><td>1.0</td><td>1.0</td><td colspan="2">B</td><td colspan="2">B/C</td><td>C</td></tr>
<tr><td colspan="9">Distilled water, pH=6.5</td></tr>
<tr><td>0.2</td><td>0.15</td><td colspan="2" rowspan="5">B</td><td colspan="2">B/C</td><td colspan="3">C</td></tr>
<tr><td>0.3</td><td>0.24</td><td>B/C</td><td colspan="2">C</td><td colspan="2" rowspan="2">C/D</td></tr>
<tr><td>0.5</td><td>0.38</td><td rowspan="2">B</td><td>B/C</td><td>C</td></tr>
<tr><td>0.7</td><td>0.59</td><td colspan="2">B/C</td><td colspan="2" rowspan="2">C</td></tr>
<tr><td>1.0</td><td>1.0</td><td colspan="2">B</td><td>B/C</td></tr>
</table>

Of all the synthesized copolymers, except for sulfonated polyacrylamide, only the CP AMPSNa and MANa has good gel-forming properties, therefore the assessment of the thermal-oxidative stability was carried out on samples of this CP with an optimal content of MANa units of 0.24 and 0.38 mole fractions. The results obtained by the DTG and DSC methods were compared with the thermal properties of the homopolymers AMPSNa and MANa, as well as the CP AMPSNa and ANa.

The first peaks observed on the DTG and DSC curves for all samples appeared in the temperature range from 68 to 89 °C and were associated with the removal of water absorbed by hydrophilic polymers from the air. It was established that in PMANa the destruction of the main chain occurs in a single step and at a higher temperature (445 ^{o}C) compared to PAMPSNa (353 ^{o}C). The decomposition of the homopolymer AMPSNa takes place in two stages with peaks at temperatures of 353 and 605 ^{o}C. The small peak at 360 ^{o}C of sodium polymethacrylate is caused by partial decarboxylation. The peak at 377 ^{o}C of sodium poly-2-acrylamido-2-methylpropanesulfonate is associated with the cleavage of part of the sulfonate groups with the release of sulfur oxides [15].

The decomposition of the main chain of copolymers occurs in two stages, starting at temperatures of 365 and 375 ^{o}C, which exceeds the decomposition temperature of the PAMPSNa chain (353 ^{o}C). The temperature indicators of the second stage of decomposition of CP AMPSNa and MANa are 500 and 550°C, which is lower than the temperature of this stage for PAMPSNa (605°C). The onset of intensive decomposition of the main chain of the CP AMPSNa and MANa occurs at lower temperatures than that of PMANa, but decomposition ends in a higher temperature region. The resistance of this copolymer to thermal-oxidative degradation is high enough that it does not decompose at reservoir temperature.

A comparison of the results of DTG of copolymers of AMPSNa with MANa and with ANa with a similar number of AMPSNa units of 0.59 and 0.63 was carried out. During the first stage of decomposition, the chain destruction temperature of CP AMPSNa and MANa is 10 ^{o}C higher than that of CP AMPSNa and ANa (385 and 375 ^{o}C), at the second stage 650 and 490 ^{o}C, respectively. The introduction of sodium methacrylic acid salt units into the copolymer instead of sodium acrylate units leads to a slight increase in the temperature at which the main chain begins to decompose and a significant rise in the temperature at which the thermal-oxidative degradation of the decomposition products is completed.

Conclusion

In this study, copolymers of sodium 2-acrylamido-2-methylpropanesulfonate with acrylamide, methacrylamide, sodium acrylate, and sodium methacrylate were synthesized. The influence of the chemical structure of the second monomer units on the ratio of units in the copolymer, chain length, interaction with polyvalent metal salts, formation of polyelectrolyte hydrogels and thermo-oxidative stability of copolymers was established. The molar ratios of units in copolymers were determined depending on the composition of the initial monomer mixture. The relative activities of the monomers were calculated. It has been shown that copolymerization of sodium 2-acrylamido-2-methylpropanesulfonate with acrylamide, methacrylamide and sodium acrylate leads to depletion, and with sodium methacrylate – to enrichment of copolymers with sodium 2-acrylamido-2-methylpropanesulfonate units. The distribution of links in the chain of all copolymers is statistical. The longest chains were formed as a result of copolymerization of sodium 2-acrylamido-2-methylpropanesulfonate with acrylamide, the shortest – with methacrylamide. Polyelectrolyte hydrogels were successfully formed through the interaction of copolymer solutions with chromium and aluminum triacetate. In addition to sulfonated polyacrylamide, the possibility of using it in the oil industry in high-temperature oil formations is not excluded for the copolymer of sodium 2-acrylamido-2-methylpropanesulfonate with sodium methacrylate. The thermal-oxidative stability of copolymers for the creation of polyelectrolyte hydrogels is sufficient so that they do not decompose at the temperature of the oil reservoir.

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