

# Polymer structure-forming agents for control the characteristics of drilling fluids

Aziza Abdikamalova<sup>1\*</sup>, Makset Kalilae<sup>2</sup>, Sarvigul Khojanazarova<sup>2</sup>, Muzaffar Khalilov<sup>3</sup>, and Shukhrat Bukharov<sup>2</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry, Tashkent, Uzbekistan

<sup>2</sup>Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan

<sup>3</sup>Karakalpak State University, Nukus, Uzbekistan

**Abstract.** Polyacrylamide and its derivatives are the most widely used industrial water-soluble acrylic polymers due to their low cost and high molecular weight. In drilling, there is a great demand for associating copolymers of acrylamide and hydrophobic comonomers. Therefore, the processes of synthesis and hydrolysis of the copolymer of acrylamide and maleic acid were studied to obtain drilling fluid stabilizers. The highest viscosity characteristics are demonstrated by samples of polymers obtained at a molar ratio of 1:7≤8. The yield of polymeric products is about 92.6, 98.1, and 96.3%, at a molar ratio of acid and acrylamide AA 1:5, 1:7, and 1:10, respectively. It has been established that an increase in the temperature of the polymer hydrolysis system contributes to an increase in the degree of conversion. Therefore, at temperatures above 80°C, an increase in yield is observed, which is primarily due to a decrease in the viscosity of the system and due to an increase in the speed of movement of polymer macromolecules. The polymer obtained in this way - MKAA-7 is characterized by higher viscosity and improved filtration characteristics compared to commercial drilling fluid stabilizers, such as hydrolyzed polyacrylonitrile, PAA and CMC (carboxymethylcellulosa).

## 1 Introduction

The main problem in increasing the stability of rock permeability and techno-economic indicators of drilling is the problem of selecting the components of the used drilling fluid and the technology of their application [1, 2]. The experience of well drilling shows that only the high quality of drilling fluids and their compliance with geotechnical conditions can increase the drilling rate, improve the quality of completion of productive layers, make full use of the technical capabilities of drilling bits and bottom-hole motor, increase their service life, reduce the cost of dealing with complications and the cost of drilling in general.

The observed progress in the chemical industry, including the production of macromolecular compounds and polymers, has contributed to their use in well construction. Polymers can be used as a stabilizer in mud fluids and as a base in polymer solutions. The first usage of such solution occurs in the mid-50s (USA). A polymer solution based on a copolymer of vinyl acetate and maleic acid contained soda ash as a pH regulator [3]. The

---

\* Corresponding author: [aziza.abdik@gmail.com](mailto:aziza.abdik@gmail.com)

polymer had flocculating and thickening properties. The first humate reagents (HR), were used as polymer drilling fluids and as a stabilizer as early as 1934 (Russia) [4].

Polyacrylamide (PAA) and its derivatives are the most widely used industrial water-soluble acrylic polymers due to their low cost and high molecular weight. The high demand is being increased for oilfield chemistry which is associated with copolymers of acrylamide and hydrophobic comonomers. Polymers of this type are considered the most promising reagents for enhanced oil recovery [5-6]. The use of polyacrylamide copolymers in polymer flooding processes in oil production [7, 8] attracts the special attention of researchers since they have improved thermal stability, resistance to high shear rates, and the presence of salts compared to high-molecular-weight AA homopolymer.

The most effective and more expensive reagent of recent years is considered to be a stabilizer of the metas type, which is a copolymer of methacrylic acid and methacrylamide. Industrial practice has shown a higher efficiency of these stabilizers compared to previously known analogs. These types of stabilizers reduce the fluid loss of both fresh and highly mineralized drilling fluids even at high temperatures (up to 250°C) at low consumption of this reagent (no more than 2%) [8].

Reagents MCY A-2 (A-3) can be used as stabilizers of drilling fluids for drilling wells under the production string. It is not recommended to process bentonite suspensions with these reagents, since they coagulate and destruct the solution [9]. Basically, PAA is obtained by free-radical polymerization of acrylamide (AA) solution in an aqueous or organic medium using azo-compounds, peroxide or redox initiators. There are homogeneous, precipitation, emulsion, suspension, and block solid-phase polymerization [10]. The most widespread is the homogeneous radical polymerization of acrylamide in an aqueous medium.

The main factors determining the abundance of this polymerization method are high rates of polymer formation and the possibility of obtaining high molecular weight polyacrylamide under these conditions.

Despite the presence of numerous studies, the tasks of developing high-quality stabilizers, as well as technologically acceptable compositions, technologies for the production of chemical reagents that are cost-effective and meet the requirements of environmental protection, remain very relevant [16,17]. In connection with the above, the purpose of the research is to improve the methods for obtaining acrylamide copolymer and experimental confirmation of their high efficiency in stabilizing clay and clayless (polymer) drilling fluids.

## 2 Materials

Acrylamide (AA) and maleic acid (MA) were chosen as the feedstock for the synthesis of co-polyacrylamide. A mixture of potassium persulfate ( $K_2S_2O_8$ ) (pure for analysis), sodium sulfite ( $Na_2SO_3$ ) (pure for analysis) in a molar ratio of 1:1.5 was used as an initiator, and sodium hydroxide was also used as a hydrolyzing agent.

For the preparation of clay drilling fluids, bentonite clay of mark "Bentonite" LLC, ПБМА, and existing commercial drilling fluid stabilizers CMC ("Efchem" LLC), gipan ("Orgsintez Plant OKA LLC"), and PAA (Navoiyazot JSC) were used.

## 3 Method

To obtain a copolymer with the required composition and structure, radical polymerization was carried out in aqueous solutions of AA and MA at pH = 7.8–7.9, since the results of early studies [11] showed that it is under such conditions that the highest yields of the copolymerization process are achieved. The polymerization process was carried out in the temperature range from 20 to 60°C and at concentrations of initiators of 0.01-0.2%. The

sequence of the synthesis process is as follows: into a four-necked round-bottom flask with a volume of 300 ml, equipped with a nitrogen purge system, a thermometer, a stirrer and a reflux condenser, 100 cm<sup>3</sup> of a solution containing 10 grams of a mixture of AA and MA, mixtures of initiators and the calculated amount of NaOH was poured to achieve pH = 7.8-7.9. The molar ratio of the starting monomers, i.e. MA and AA varied from 1:5 to 1:10, while the pH of the solutions reached values from 1.65 to 2.18.

The resulting reaction mass was blown out with nitrogen to remove air from the system, the pressure in the reaction vessel was regulated by feeding certain amounts of nitrogen. The mixture was kept in a thermostat for 1-6 hours at a certain temperature and constant stirring.

The synthesized polymer was isolated from the reaction medium by adding acetone in portions at room temperature until its complete sedimentation was achieved. The sediment was separated from the liquid medium, washed with acetone, and dried in vacuum to constant weight, and the yields and composition of the polymer were determined. The residual content of the monomer was determined by the bromide-bromate method [12]

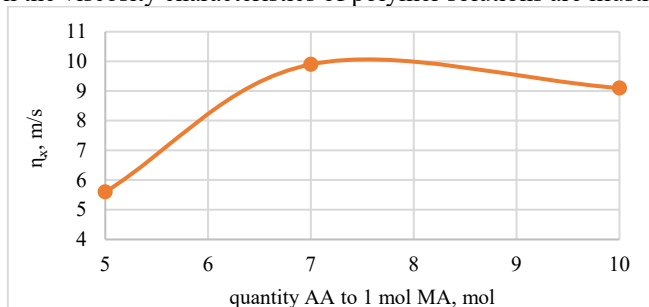
To increase the water solubility and improve the structure-forming abilities of the synthesized polymer samples, alkaline hydrolysis processes were carried out. Factors influencing the degree of hydrolysis were studied: temperature (from 50 to 98°C), process duration (from 0.5 to 3 h) and consumption of the hydrolyzing agent (in a molar ratio with monomers from 1:1 to 1:2).

The kinetics of hydrolysis was controlled by the potentiometric method. The degree of hydrolysis was determined by sampling in the amount of 2 ml, which was subjected to potentiometric titration. The acid number (AN) was determined by back titration of the polymer solution and its hydrolysis product. According to the found values of the acid number, it was discussed the change in the number of carboxyl groups during the hydrolysis of the initial copolymers. The nitrogen content in polymers was determined by the generally accepted Kjeldahl method using the K9840 Automatic Kjeldahlm Distillation Unit.

The specific viscosity ( $\eta_{sp}$ ) of solutions of polymer samples was determined by using an Ostwald viscometer at a temperature of 25°C depending on the concentration. For this, appropriate solutions were prepared with different concentrations (0.50-0.01 g/100 ml) by dilution with water or 0.1 N solution KCl. Characteristic viscosity ( $\eta_x$ ) of AA solutions was determined graphically from the dependence of  $\eta_{sp}$  on concentration C ( $\eta_{sp}/C$ ).

## 4 Result and discussion

A change in the molar ratio of the reacting monomers strongly affects the viscosity characteristics of the obtained polymers. The viscosity of polymer solutions is usually related to the molecular weight distribution and the number of functional groups involved in the formation of the coagulation structure. The results of studying the influence of the molar ratio of monomers on the viscosity characteristics of polymer solutions are illustrated in Figure 1.



**Fig. 1.** Dependence of the viscosity of copolymer solutions on the ratio of monomers.

As can be seen from the figure, the highest viscosity characteristics are demonstrated by polymer samples obtained at a molar ratio of  $1:7 \leq 8$ . The change in viscosity characteristics with a change in the molar ratio of the initial monomers of the reaction is associated with the nature of the macromolecule and its volume. The resulting copolymer usually consists of various microblocks: blocks of polyacrylamide, blocks of maleic acid, blocks of AA and maleic acid. The ratio of these blocks in a macromolecule is related to the activity coefficient of the monomers. The Feynman-Ross method was used to estimate the relative activities of monomers [13]. As a result, it was found that the mole fractions of MA in the copolymer are 0.31; 0.33; 0.34 and 0.35 at a molar ratio of MA and AA, respectively, 1:5, 1:7, 1:8 and 1:10. According to the data obtained, activity values were found, which are 0.96 and 0.10 for MA and AA. These data show that the activity of MA in polymerization reactions is much higher than that of AA. At the initial moment of the reaction, one should expect an increase in the share of UA in the resulting product [14] and its depletion in AA units. An increase in the proportion of MA in the system leads to an excessive increase in MA-MA blocks; it is known that a few MA molecules can bind to each other (generally, the degree of polymerization does not exceed 10) and form oligomers [15]. Probably, due to this, the yield of the polymer product and the viscosity characteristics of their solutions are significantly lower with an increase in the mole fraction of MA in the reaction mixture.

The comparative decrease in viscosity with an increase in the mole fraction of AA (more than 8 mol per 1 mol of MA) is probably not associated with a decrease in molecular weight, but with a decrease in the proportion of structure-forming COOH and COONa groups along the macromolecule chain.

Precipitation in the acetone system shows the yield of polymer products of about 92.6, 98.1 and 96.3%, at a molar ratio of MA and AA 1:5, 1:7 and 1:10, respectively. It was the sample of the copolymer of MA and AA (MKAA-7) obtained at a molar ratio of 1:7 that was taken for further research.

It is known that in the process of alkaline hydrolysis of PAA and other AA copolymers, there is an effect of adjacent units, that is, the effect of reacted functional groups in a macromolecule on the reactivity of adjacent groups. As a result, the reactivity of the functional groups may change with the degree of conversion. As the hydrolysis yield increases, amide groups are blocked by two neighboring ionized carboxyl groups, which leads to incomplete alkaline hydrolysis of the polymer (under normal conditions, the degree of conversion does not exceed 70%) and slows down the reaction rate. It has been established that an increase in the temperature of the polymer hydrolysis system contributes to an increase in the degree of conversion. So, at temperatures above 80°C, an increase in yield is observed, which is primarily due to a decrease in the viscosity of the system, due to an increase in the speed of movement of polymer macromolecules. Probably, due to diffusion processes, the possibility of collision of hydrolyzing agents and unreacted amide groups increases.

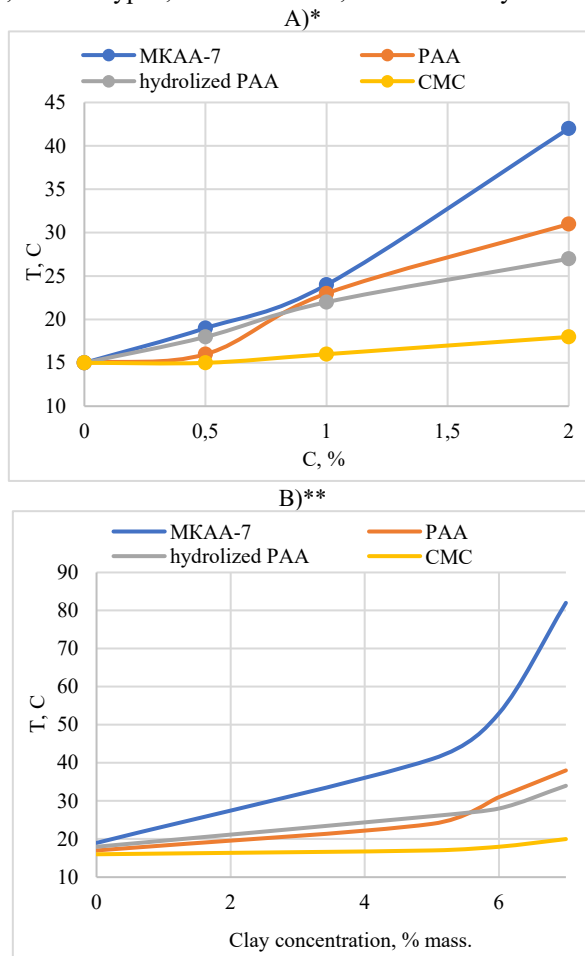
**Table 1.** Effect of hydrolysis time on the composition and characteristics of MKAA-7 (hydrolysis temperature 60°C).

| T, h | C <sub>N</sub> , % | Degree of hydrolysis, % | AN, mg NaOH/g |
|------|--------------------|-------------------------|---------------|
| -    | 15.97              | 0.00                    | 201           |
| 0.5  | 14.61              | 11.18                   | 286           |
| 1    | 12.96              | 30.11                   | 356           |
| 1.5  | 12.1               | 41.25                   | 376           |
| 2    | 10.26              | 48.49                   | 387           |
| 3    | 9.21               | 53.12                   | 357           |

(T is the duration of hydrolysis; AN is the amount of nitrogen in the polymer)

Up to 1.5 hours of the hydrolysis process, an increase in the AN of the obtained polymers is observed, which indicates the formation of new acid groups, i.e., carboxyl groups due to the transformation of amide groups in the polymer. The continuation of the process does not significantly increase the AN values, and after a 2-hour hydrolysis, the values of this indicator in the samples decrease, which is probably related to a decrease in the amount of free carboxyl groups due to their transition to the COONa form as a result of hydrolysis in an alkaline medium. Therefore, just these samples that should exhibit increased structure-forming abilities when processing clay and clay-free drilling fluids.

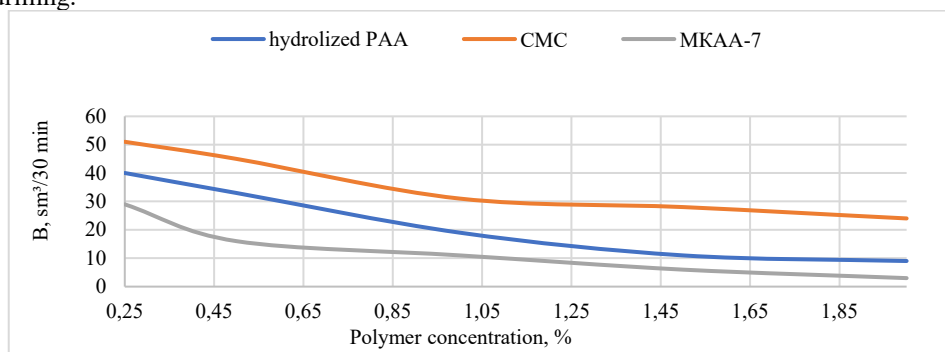
In drilling practice, the regulation of the processes of structure formation and stability of clay suspensions is carried out with the help of chemical reagents. The main goal of the chemical treatment of drilling fluids is to achieve the required technological, structural and mechanical properties, with a minimum consumption of chemical reagents. In studies, the characteristics of the obtained polymeric stabilizer were compared with the reagents existing in drilling practice, such as hypan, PAA and CMC, which differ by nature and characteristics.



**Fig. 2.** Influence of concentration. A) stabilizers; B) clays on the relative viscosity of their suspension. \*-concentration of clay 5% of the mass; \*\*-concentration of stabilizers 0.5% wt.

As the curves of the diagram show, solutions based on the MKAA-7 sample have higher values of relative viscosity compared to other studied stabilizers at the same contents in the solution. Solutions of hydrolyzed PAA (pH=8) at low concentrations are characterized by

relatively low values of relative viscosity, however, an increase in concentration of more than 1% slightly increases the value of viscosity, and their values exceed hypan solutions, which indicates high structure-forming hydrolyzed forms of the synthesized acrylamide polymers. Due to this, the use of the synthesized copolymer in clay suspensions makes it possible to reduce the clay content in them, which also favors an increase in the speed of mechanical drilling.



**Fig. 3.** Change in fluid loss (B) of 5% clay suspensions from the content of the stabilizer at 40°C.

A comparative analysis of the obtained curves of the dependence of the conditional viscosity on the content of clay in the composition of the drilling fluid shows that the stabilizing effect of the use of polymeric materials depends on the content of the solid phase in suspensions, the more clay particles in the volume, the greater the positive effect in the form of an increase in the viscosity of the drilling fluid.

One of the main technological characteristics of flushing fluids is their filtration performance. Unique structural-rheological properties and filtration performance ensure minimal penetration of drilling fluid into the formation. Low fluid loss, especially at high temperatures, is a key factor in successful completion of the well. The results of the study of the effects of polymer stabilizers on the system's fluid loss are illustrated in fig. 3. As can be seen from the figure, the lowest fluid loss values are characteristic of a 5% suspension of clay treated with MKAA-7. A stabilizing effect is already observed at a concentration of 0.5%. Increasing the concentration to 2% reduces the values of B to 3-4 cm<sup>3</sup>/30 min, while commercial hydrolyzed polyacrylonitrile reduces only to 10 cm<sup>3</sup>/30 min. Thus, the thermal stability and stabilizing effect of MKAA-7 is achieved by higher molecular weight values, higher molecular weight distribution characteristics, and the presence of sufficient amounts of functional groups (carboxylate, carboxyl) that are involved in the formation of a spatial structure in the system of clay and clay-free drilling fluids. Hydrolyzed polyacrylonitrile and synthesized MKAA-7 mainly differ in average molecular weight values, which are 1800 and 2600 kDa, respectively. Hydrolyzed polyacrylonitrile contains oligomers weighing 1200-300 Da in an amount of about 40%, while for MKAA-7 oligomeric compounds do not exceed 8-10%.

## 5 Conclusion

The processes of synthesis of a new polymeric structure-forming reagent based on AA and maleic acid have been studied. It has been established that high yields of the macromolecule are achieved at a molar ratio of AA and MA of 7:1 at a temperature of 70-80°C. The hydrolysis of the resulting polymer should be carried out at a temperature of at least 60°C for 2.5-3 hours. Especially, under such conditions, the degree of hydrolysis reaches 54-55%, and the acid number of the product decreases to 357. It is under such conditions that the degree of hydrolysis reaches 54-55%, and the acid number of the product decreases to 357. The

resulting polymer sample demonstrated better stabilizing characteristics of clay suspensions compared to commercial stabilizers such as PAA, Hydrolyzed polyacrylonitrile, CMC, namely, higher values of viscosity characteristics with a maximum reduction in system fluid loss. Thus, the thermal stability and stabilizing effect of MKAA-7 is achieved by higher molecular weight values, higher molecular weight distribution characteristics, and the presence of sufficient amounts of functional groups (carboxylate, carboxyl) that are involved in the formation of a spatial structure in the system of clay and clay-free drilling fluids.

## References

1. Kh. M. Islamov, Scientific Works of the Nakhchivan State University **3**, 30-33 (2014)
2. Yu. M. Basarygin, A. I. Bulatov, Yu. M. Proselkov, *Well completion* (Nedra-Businesscenter, M., 2002), 454-455
3. J. Gray, G. Darley, *Composition and properties of drilling agents (flushing fluids)* (Nedra, M., 1985), (509)
4. V. Ovchinnikov, N. Aksenova, L. Kamenski, V. Fedorovskaya, *Drilling and oil* **12**, 24-29 (2014)
5. K. C. Taylor, H. A. Nasr-El-Din, *J. Pet. Sci. Eng.* **19**, 265-280 (1998)
6. Yu. A. Shashkina, Yu. D. Zaroslov, V. A. Smirnov, *Polymer* **44(8)**, 2289-2293 (2003)
7. R. O. Afolabi, *American Journal of Polymer Science* **5(2)**, 41-46 (2022)
8. H. Chen, H. Tang, X. Wu et al, *Journal of Dispersion Science and Technology* **37(4)**, 486-495 (2015)
9. A. I. Bulatov, P. P. Makarenko, Yu. M. Proselkov, *Drilling, flushing and grouting solutions. Proc. Allowance for universities* (Nedra, M., 1999), 31-33
10. N. A. Petrov, *Electronic scientific journal "Oil and Gas Business"* **3**, 37-65, (2016)
11. V. A. Kargin, *Encyclopedia of polymers: encyclopedia* **1** (Soviet Encyclopedia, Moscow, 1972)
12. S. O. Tileubaev, M. U. Kalilaev, A. B. Abdikamalova, I. D. Eshmetov, A. M. Reymov, *Science and Education in Karakalpakstan* **3**, 138 -142 (2021)
13. Yu. D. Semchikov, *Vysokomolekulyarnye soedineniya [High- molecular compounds]. N. Novgorod: Nizhegorodskiy gosudar- stvennyy universitet im. N. I. Lobachevskogo Publ.* (Akad- emiya Publ., M., 2003)
14. L. B. Yakimova, D. V. Kyivitskaya, *Journal of the Belarusian State University. Chemistry* **1**, 76-82 (2018)
15. Dongzhong Chen, Charles Q. Yang, Xiaoqun Qiu, *Aqueous Polymerization of Maleic Acid and Cross-Linking of Cotton Cellulose by Poly (maleic acid) Ind. Eng. Chem. Res.* **44**, 7921-7927 (2005)
16. R. M. Usmanov, I. D. Eshmetov, R. J. Eshmetov, A. I. Sharipova, S. Kuldasheva, *Journal of Critical Reviews* **7(12)**, 128-135 (2020)
17. S. Kuldasheva, B. Jumabaev, A. Agzamkhodjayev, L. Aymirzaeva, K. Shomurodov, *Journal of Chemical Technology and Metallurgy* **50(3)**, 314-320 (2015)