***Synthesis of acrylamide copolymers with improved viscosity characteristics***

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**Abstract:** The prerequisite for this study was the influence of the pH of the medium on the copolymerization process and the characteristics of the copolymers of itaconic acid and acrylamide. The aim of the work was to study this effect on the molecular weight of copolymers and their yield. The methodology included copolymerization of IR and AA at different pH values and different mole ratios of monomers, as well as analysis of the molecular characteristics of copolymers and product yield. The obtained data demonstrate that copolymers synthesized under neutral and slightly alkaline conditions have higher molecular weights and yields compared to an acidic medium, which opens up new prospects for tuning the synthesis of copolymers with desired properties.

**Keywords:** copolymerization, itaconic acid, acrylamide, pH of the medium, molecular weight, product yield.

**Introduction**

Water-soluble polymers, derivatives of acrylamide, known as polyacrylamides (PAA), are widely used in various fields of industry and agriculture [1, 2]. They have found their application as effective flocculants for the purification of drinking and wastewater [3], as well as in reverse osmosis membranes [4]. In addition, polyacrylamides are used to stabilize emulsions and suspensions, and in the oil industry - as stabilizers of drilling fluids [5] and additives that reduce hydraulic resistance [6] during transportation through pipelines. These polymers are also used in construction and mineral processing.

The synthesis of polyacrylamide and its copolymers with acrylamide is most often carried out through homogeneous polymerization of acrylamide in an aqueous solution using water-soluble initiators such as ammonium, potassium or sodium persulfates. Modern research is actively studying the effect of mixed initiator systems on the properties of polyacrylamide, as well as polymerization reactions in more concentrated monomer solutions [7].

But not only polyacrylamide, but also its modifications and copolymers with unsaturated acids, have found application in science and industry. They successfully replace polyacrylamide as flocculants, thickeners and structure-forming agents [16]. The researchers' interest in copolymers obtained through radical copolymerization of acrylamide with unsaturated acids, including itaconic acid [17] is due to the high yield of high-molecular compounds using concentrated monomer solutions [18-20]. It is important to note that most studies on the synthesis of these copolymers have been conducted in organic media and aqueous organic emulsions. Therefore, it is important to conduct further research in the direction of synthesis of these copolymers in an aqueous medium.

**The experimental part**

In the study, high purity acrylamide (more than 99.0%, Servicebio supplier) and itaconic acid (also more than 99.0% purity, Sigma Aldrich supplier) were used to synthesize the acrylamide copolymer. All experiments were carried out using the following reagents: bidistilled water, acetone, potassium persulfate (K2S2O8), sodium sulfite (Na2SO3), potassium chloride (KCl), potassium hydroxide (KOH) and hydrochloric acid (HCl). The molecular weights of the obtained polyacrylamides were determined by gel chromatography on an Agilent 1260 Infinity liquid chromatograph equipped with a refractometric detector and a TSK GM PWXL column. The viscosity of polymer solutions was measured at a temperature of 25 ° C using an Ostwald viscometer, according to the method described in the source [9].

An equimolar ratio of potassium persulfate and sodium sulfite was used as the initiator of polymerization, which is described in the literature [10]. The polymerization process was carried out at various temperatures and concentrations of the initiator, strictly observing the stoichiometric proportions of persulfate and sulfite. The synthesis procedure included the stages of purging the reaction mixture with nitrogen, maintaining a set temperature in a thermostat with constant stirring, as well as precipitation of the polymer when acetone was added. To remove impurities, the precipitate was repeatedly washed with acetone and then dried under vacuum, which made it possible to evaluate the yield and characteristics of the synthesized copolymers.

**Results and their discussion**

Our previous studies [13] have shown that for polymerization of acrylamide (AA) with an optimal monomer content in the reaction system of 10%, the mass of the initiating mixture should not exceed 0.1% of the mass of the monomer. The polymerization temperature should be maintained at 45 ± 1 °C, since under these conditions the maximum viscosity values of polyacrylamide solutions are reached. The introduction of itaconic acid into the reaction system has a significant effect on the kinetics of the polymerization process of acrylamide. Unlike conventional polymerization of acrylamide, copolymerization should be carried out at a higher temperature, at least 45-50 ° C, and this is primarily due to an increase in the viscosity of the reaction medium. Similar results were obtained during copolymerization of AA with other unsaturated acids [13, 22, 23]. Probably, the increase in viscosity is associated with a change in the state of macromolecules and an increase in the number of functional groups along the chain that participate in structure formation in the system and lead to an increase in viscosity [13, 23-25]. To ensure a high yield in a higher molecular weight copolymer, the process temperature should be at least 50°C.

In the course of early experiments, a decrease in the yield of AA polymerization was recorded at a temperature exceeding 45 °C, which is associated with an increase in the proportion of acrylamide conversion products with a lower molecular weight and oligomeric forms. To ensure a high yield of polymer macromolecules in the system, the ratio of AA to the sum of K2S2O8 and Na2SO3 should be maintained at 0.05, which corresponds to about 0.1%. The effect of a mixture of initiators has an almost similar effect on the process of copolymerization and polymerization of AA [13]. At concentrations of the components of the initiating system at the level of 0.05%, copolymers with a higher molecular weight can be obtained, however, as the experimental results have shown, this requires an increase in the duration of the process (more than 4.5 hours versus 3 hours for AA polymerization). However, an increase in the initiator concentration from 0.05% to 0.15% (by weight of monomers) contributes to an increase in the polymerization rate, maintaining this rate for a longer time and reducing the process time from 4.5 to 2.5-3 hours. This also leads to an increase in the copolymerization yield from 84.5 to 95.9%.

During copolymerization, with an initiator consumption of 0.1%, a dense, homogeneous and transparent product is formed with a pH level of 2.11, which is achieved with a ratio of the initial monomers of itaconic acid to acrylamide of 1:5. An increase in the proportion of acrylamide to 10 mol per mol of itaconic acid leads to a slight increase in pH by 0.07 points. Under such conditions, in contrast to the process of obtaining pure polyacrylamide, the copolymers turn out to be easily soluble in water.

It was found that an increase in the content of itaconic acid in the reaction mixture leads to a decrease in the copolymer yield, which is illustrated in Fig. 1. It is assumed that this is due to the formation of complexes between itaconic acid monomers and acrylamide in an acidic medium, which, due to hydrogen bonds and other interactions, are poorly involved in copolymerization [14]. It is also known that itaconic acid, along with other unsaturated acids such as methacrylic and fumaric acids, is poorly subjected to radical homopolymerization due to significant electron acceptor and steric influences due to the close location of carboxyl groups [15]. It is assumed that such interactions lead to a decrease in the amount of high-molecular product and an increase in the proportion of low-molecular and oligomeric products in the system.

The highest copolymer yield and viscosity are observed with the ratio of itaconic acid monomers to acrylamide in the range from 1:5.5 to 1:6.0, while the yield reaches approximately 96.81%, as shown in Fig. 1. This copolymer has been labeled as 1AA:IR-5.5. The main substance in the resulting product was at least 99.1% by weight, and the polymer itself had a light yellow or almost white color.

Fig. 1. Dependence of the copolymer yield at different IR values:AA.

In order to study the effect of the pH of the medium on the characteristics of the process and the characteristics of the obtained copolymers, subsequent experiments on the copolymerization of itaconic acid (IC) with acrylamide (AA) were carried out under similar conditions, but with the preliminary creation of a slightly alkaline medium (pH = 8) by adding a 10% solution of sodium hydroxide (NaOH). As a result of copolymerization of IR and AA in a molar ratio of 1:5.5, a dense, transparent and homogeneous mass was formed. The extraction process of the resulting copolymer was similar to the previous method. The yield of the product was 99.12%, surpassing the results obtained with the molar ratios of IR and AA 1:4 and practically comparable to the ratio of 1:10. This sample of the copolymer was conventionally named 2AA:IR-5.5.

Studies have confirmed that exposure to the pH of the medium has a strong effect on the yield of the copolymerization reaction in comparison with the polymerization of acrylamide. For example, the synthesized polymer AA at pH = 8.1 had an almost identical molecular weight compared to the reaction at pH = 2.4 [13], however, its yield in the form of polymer products insoluble in acetone was 94.5%, while in an acidic medium this yield was 85.8%. These data show that an increase in the concentration of OH ions in the reaction mixture changes the kinetics of the process, increases the initial reaction rate and sharply increases the yield of the copolymerization reaction in the initial stage [21].

The synthesis processes were performed in an environment with a high pH value of 11. A certain amount of NaOH was used to achieve the neutralization of carboxyl groups and partial hydrolysis of amide functions. During copolymerization, the formation of a homogeneous, transparent and dense polymer mass was recorded. The copolymer extraction process did not differ from the methods used earlier. Under these conditions, an increased yield of copolymers and an increase in viscosity were also achieved with a molar ratio of the initial monomers of 1:5÷6, while the copolymer yield reached 95.87%. This sample has been identified as 3AA:IR-5.5.

Fig. 2. Dependence of the viscosity of copolymer solutions on the ratio of monomers.

The graph in Fig. 2 shows the dependence of the viscosity of copolymer solutions on the ratio of acrylamide (AA) monomers to itaconic acid (IC).

It can be seen from the graph that with an increase in the AA ratio/IR, the viscosity of solutions of all three copolymers increases. This increase in viscosity is most noticeable in the range from 1:1 to about 1:5 mole of acrylamide per mole of itaconic acid. After reaching a ratio of 1:5, the curves are aligned, and the viscosity of the solutions changes insignificantly with a further increase in the acrylamide content.

The curves for 1AAIK and 2AAIK show similar trends, with the 2AAIK curve being slightly higher over the entire range of ratios. This may indicate a slightly higher viscosity of 2AAIC copolymers compared to 1AAIC at the same AA/IR ratios. The curve for 3AAIC starts with a lower viscosity at a 1:1 ratio, but then coincides with the trend of the other curves, showing a similar increase in viscosity with an increase in the AA/IR ratio.

Based on the graph, it can be concluded that the optimal ratio of monomers to achieve maximum viscosity of copolymer solutions is in the region of 1:5-1:6 mol of acrylamide per mol of itaconic acid. This ratio corresponds to the best polymer yield and viscosity.

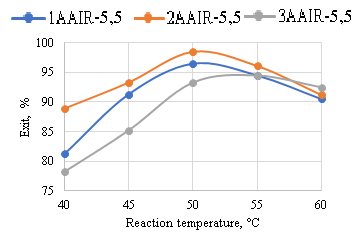


Fig. 3. Dependence of the reaction output on the system temperature.

An analysis of the data in Fig. 3 of the dependence of polymer yields on temperature in general shows that with increasing reaction temperature, the yield of all three copolymers increases (1AA:IR-5.5, 2AA:IR-5.5, 3AA:IR-5.5).

At lower temperatures (40 and 45°C), copolymer yields are significantly lower compared to higher temperatures, especially for 1AA:IR-5.5. This may be due to the slow kinetics of the reaction at low temperatures.

Nevertheless, despite the increase in copolymer yields compared to the PAA production process [13], the time of this process is quite long, at least 3.5-4.0 hours. The obtained copolymers are characterized by higher values of viscosity characteristics, which is due to the higher molecular weight of copolymers based on itaconic acid and acrylamide (Table 1).

*\*The molecular weight of the components of the AA and IR copolymer system (AA/IR = 5.5) and their process duration is 4 hours, the initial concentration of monomers is 10%, the amount of initiator is 0.1%.*

|  |  |  |
| --- | --- | --- |
| Copolymer | The molecular weight of the reaction products, kDa | The content in the system, % by weight. |
| 1АА:IR-5,5 | 2700-2800  166  12-15 | 85  13  ~2 |
| 2АА:IR-5,5 | 2900-3000  60  ~1 | 92  6  ≤2 |
| 3АА:IR-5,5 | 2500-2600  3-5 | 89  11 |

The presented table summarizes the results of the synthesis of copolymers. Copolymerization was carried out for four hours at an initial concentration of 10% monomers with the addition of an initiator in a volume of 0.1%. Sample 1AA:IR-5.5 demonstrates the molecular weight of copolymers in the range of 2700-2800 kDa. For sample 2AA:IR-5.5 molecular weight ranges between 2900 and 3000 kDa. Option 3AA:IK-5.5 shows the lowest molecular weight values in the range of 2500-2600 kDa. At the same time, the 3AA system:IK-5.5 is distinguished by a higher percentage of polymers in comparison with the 1AA system:IR-5.5, where the proportion of copolymers is 85%. The maximum content of copolymers was found in the 2AA system:IR-5.5, reaching 92% of the total weight, while the remaining part is attributed to oligomers with a lower molecular weight. It is obvious from the data in the table that different copolymers are characterized by diversity both in molecular weight and in percentage content in the system. For example, 2AA:IK-5.5 has the largest molecular weight and the highest percentage, whereas 3AA:IK-5.5 has the lowest molecular weight, but the proportion of polymers is comparable to 1AA:IR-5.5.

**Conclusion**

In conclusion of this study, it can be noted that the copolymerization of acrylamide with itaconic acid showed the dependence of the properties of synthesized polymers on many factors, including the pH of the medium, the ratio of monomers and polymerization conditions. It was found that the optimal conditions for obtaining copolymers with high yield and good viscosity characteristics correspond to a medium with a pH of about 8.1 and a molar ratio of itaconic acid to acrylamide in the range of 1:5.5 to 1:6.0. At the same time, the copolymer yield reaches approximately 96.81%, and the mass fraction of the main substance in the product is at least 99.1%.

Experiments in highly alkaline media with pH 11 also showed positive results with a copolymer yield of 95.87% and characteristics due to the required amount of NaOH for the neutralization of carboxyl groups and partial hydrolysis of amide groups. The observed formation of a dense, transparent and homogeneous polymer mass indicates the success of the synthesis technique used.

Gel chromatographic analysis revealed differences in the molecular weight of the copolymers, ranging from 2500 to 3000 kDa depending on the ratio of the initial monomers, which emphasizes the influence of the composition of the reaction mixture on the molecular characteristics of the copolymers. The high molecular weight indicates the formation of long-chain polymer structures, which, in turn, affects the viscosity and mechanical properties of polymers.

**References**

1. Alnuaimi, Ghuwaya Humaid, "Synthesis and Solution Characterization of Water-Soluble Polyacrylamide and Its Applications in Oil Industries" (2005). Theses. 384. <https://scholarworks.uaeu.ac.ae/all_theses/384>
2. Sharipova, A.A.; Aidarova, S.B.; Mutaliyeva, B.Z.; Babayev, A.A.; Issakhov, M.; Issayeva, A.B.; Madybekova, G.M.; Grigoriev, D.O.; Miller, R. The Use of Polymer and Surfactants for the Microencapsulation and Emulsion Stabilization. Colloids Interfaces 2017, 1, 3. <https://doi.org/10.3390/colloids1010003>.
3. Kasgoz, Hasine & Özgümüş, Saadet & Orbay, Murat. (2003). Modified polyacrylamide hydrogels and their application in removal of heavy metal ions. Polymer. 44. 1785-1793. 10.1016/S0032-3861(03)00033-8.
4. Demirbas, O., Turhan, Y. and Alkan; MThermodynamics and kinetics of adsorption of a cationic dye onto sepiolite. Desalination and Water Treatment, 54 (3), 707-714. (2015).
5. Investigation of inhibitory characteristics of polymer drilling fluids // Universum: technical sciences : electron. scientific. journal. Tileubaev S.O. [et al.]. 2022. 5(98). URL: https://7universum.com/ru/tech/archive/item/13697 (accessed: 08.01.2023).
6. R.P.Singh, S.K.Jain and N.Lang, in: Polymer Science Contemporary Themes, S. Sivarm (Ed.), Tata McGraw-Hill, New Delhi, Vol.II, p.716, 1991.
7. Nedal Y. Abu-Thabit. Thermochemistry of Acrylamide Polymerization: An Illustration of Auto-acceleration and Gel Effect. World Journal of Chemical Education. 2017; 5(3):94-101. doi: 10.12691/wjce-5-3-3
8. Sáez-Plaza, Purificación & Navas, María & Wybraniec, Sławomir & Michałowski, Tadeusz & Garcia Asuero, Agustin. (2013). An Overview of the Kjeldahl Method of Nitrogen Determination. Part II. Sample Preparation, Working Scale, Instrumental Finish, and Quality Control. Critical Reviews in Analytical Chemistry. 43. 10.1080/10408347.2012.751787.
9. GOST 11034-82 polyamides. Method for determining the number of viscosity of dilute solutions.
10. Kurenkov V.F., Verizhnikova A.S., Myagchenkov V.A. Features of inversion emulsion polymerization of acrylamide in the presence of Tuon and the initiating system K2S2O8-Na2S2O5. High-molecular compounds. Vol. XXVIII. 1986. No. 3. pp. 488-492.
11. Tileubaev S.O., Kalilaev M.U., Abdikamalova A.B., Eshmetov I.D. The influence of stabilizers on the technological characteristics of clay drilling fluids // Universum: chemistry and biology: electron. scientific. journal. 2021. No. 8(86). pp. 41-45.
12. Tileubaev S.O., Abdikamalova A.B., Kalilaev M.U., Eshmetov I.D. Synthesis of stabilizers of drilling fluids based on acrylamide and their stabilizing effect // International scientific - online conference on innovation in the modern education system. USA. May 25, 2022. – pp. 295-301.
13. Kuldasheva, S., Abdikamalova, A., Eshmetov, I. et al. Investigation of changes in the viscosity properties of acrylamide (co)polymer and their hydrolyzed forms depending on the conditions of their preparation. Polym. Bull. (2023). <https://doi.org/10.1007/s00289-023-04875-6>
14. Asanov A.A., Pogorelsky K.V., Sharipova A.I. Development of colloidal-chemical bases for obtaining a new water-soluble polymer-soil structurizer //Tez. dokl. 2nd Scientific Conference of young scientists and specialists "Fertilizers-95". Tashkent, 1995. - p. 68.
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. 2005, 44, Pp. 7921-7927.
16. Faridi, S., Mobinikhaledi, A., Moghanian, H. *et al.* Synthesis of novel modified acrylamide copolymers for montmorillonite flocculants in water-based drilling fluid. *BMC Chemistry* **17**, 125 (2023). <https://doi.org/10.1186/s13065-023-01042-w>
17. P. Lanthong, R. Nuisin, S. Kiatkamjornwong, Graft copolymerization, characterization, and degradation of cassava starch-g-acrylamide/itaconic acid superabsorbents, Carbohydrate Polymers, Volume 66, Issue 2, 2006, Pages 229-245, <https://doi.org/10.1016/j.carbpol.2006.03.006>.
18. Chen, Z., Liu, M., & Ma, S. (2005). Synthesis and modification of salt-resistant superabsorbent polymers. \*Reactive and Functional Polymers, 62\*(1), 85-92. <https://doi.org/10.1016/j.reactfunctpolym.2004.09.003>
19. Karadağ, E., Üzüm, Ö. B., & Saraydin, D. (2005). Water uptake in chemically crosslinked poly(acrylamide-co-crotonic acid) hydrogels. \*Materials & Design, 26\*(4), 265-270. <https://doi.org/10.1016/j.matdes.2004.07.014>
20. Teleky BE, Vodnar DC. Biomass-Derived Production of Itaconic Acid as a Building Block in Specialty Polymers. Polymers (Basel). 2019 Jun 11;11(6):1035. doi: 10.3390/polym11061035. PMID: 31212656; PMCID: PMC6630286.
21. H.Kheradmand, J.François, V.Plazanet. Hydrolysis of polyacrylamide and acrylic acid-acrylamide copolymers at neutral pH and high temperature // Polymer, Volume 29, Issue 5, 1988, Pages 860-870, <https://doi.org/10.1016/0032-3861(88)90145-0>.
22. Sharipova A.I., Asanov A.A., Sirlibaev T.S. The structure-forming effect of a water-soluble polyelectrolyte based on maleic acid and acrylamide //Uzbek Chemical Journal. Tashkent. Fan. 1999. No. 1. pp. 24-26.
23. Akhmedov K.S., Sharipova A.I., Asanov A.A. and others. The influence of the pH of the medium on the structure-forming effect of polyelectrolyte based on maleic acid and acrylamide // DAN RUz. 1998. No. 12. pp. 29-31.
24. A.A. Lipin, A.V. Shibashov, A. G. Lipin. Modeling of the polymerization process of acrylamide in concentrated aqueous solutions // Izvestiya vuzov. Chemistry and chemical technology. - 2014. - Vol. 57, vol. 12. - pp. 85-87.
25. Ivanov V.A., Kamenshchikov A.F., Gromov V.F., Kaminsky V.A., Bune E.V., Mathematical modeling of the polymerization process of acrylamide in concentrated aqueous solutions // High-molecular Compounds, Volume 34, No. 9, 1992. – pp. 15-21.