

## CONTROL OF CONFORMATIONAL STRUCTURES OF POLYACRYLAMIDE MACROMOLECULES

T.V. Shevchenko, Yu.V. Ustinova, E.O. Ermolaeva\*, D.M. Borodulin

Kemerovo State University, Kemerovo, Russia

**Abstract.** The purpose of the study is to propose a variant of the polyacrylamide modification mechanism with the use of serine. Methods: determination of the molecular weight of polyacrylamide macromolecules was calculated using the Mark-Houwink equation. Results: The paper presents the results of the study on the development of accessible ways to control the conformational structures of high-molecular compounds on the example of polyacrylamide. The authors propose a technological and affordable method for fixing and preserving conformational structures of macromolecules based on modification processes with the use of low-molecular compounds containing two active functional groups (chlorohydrins, glycols, or amino acids). Modification schemes and basic physicochemical properties of modified structures are presented. Based on the analytical review and results of the study, it was found that the processes of controlling the conformational structures of high-molecular compound macromolecules had not been sufficiently studied. It was established that the main available, technologically simple, but insufficiently effective method of carrying out conformational changes in polyacrylamide macromolecules was the process of its hydration.

**Keywords:** polyacrylamide, swelling, volumetric dimensions, viscosity, modifiers, chlorohydrins, glycols, amino acids.

**Corresponding Author:** E.O. Ermolaeva, Kemerovo State University, 6 Krasnaya Street, Kemerovo, 650000, Russia, e-mail: [ermolaeva.e.o@mail.ru](mailto:ermolaeva.e.o@mail.ru)

**Received:** 21 April 2022;

**Accepted:** 30 June 2022;

**Published:** 1 August 2022.

### 1. Introduction

The largest number of natural materials are high-molecular compounds (HMCs), the properties of which differ significantly from the properties of low-molecular compounds. HMC macromolecules have flexible chains with rotary isomerism (conformation) due to the rotation of individual chain links (Wang *et al.*, 2018; Joshi & Abed, 2017; Kitahara *et al.*, 2012). They are characterized by special rheological properties and a special dependence of shear stresses on the deformation rate (non-Newtonian fluids).

There are several types of conformations: an equilibrium stable (inhibited) conformation with the average energy of the system under these conditions and an active (obscured) conformation with increased binding energy due to the supply of external energy. By changing the conformational properties of macromolecules, it is possible to obtain an HMC with new properties (Shevchenko, 2004; Ustinova *et al.*, 2008).

Polyacrylamide (PAA) is an important technical high-molecular product (floculant) widely used for the treatment of microheterogenic wastewater of various compositions and nature. It has a high molecular weight (MW) (20 to 40 million) and a certain chemical composition (Gholami *et al.*, 2020; Dai *et al.*, 2015; Chen *et al.*, 2021).

PAA molecules, due to the presence of carboxyl and amine groups, represent a simplified model of a protein macromolecule, based on which extensive research is carried out to study the properties of protein materials. During hydrolysis of PAA macromolecules in an alkaline medium, anionic systems are formed, while interaction with acid results in the formation of cationic systems (Karam *et al.*, 2021; Bolto & Gregory, 2007; Liu *et al.*, 2021).

The modification mechanism is based on obtaining cross-linked spatial unfolded macromolecular chains of the selected PAA under certain conditions in the presence of modifiers due to the formation of hydrogen or covalent bonds between functional groups of macromolecules and modifiers (Mao *et al.*, 2021; Yu *et al.*, 2021; Naruka *et al.*, 2021).

For modification, there are chemically active organic modifiers with a small carbon chain, belonging to the class of glycols and the class of chlorohydrins. The preparation of PAA solutions from PAA powders included a swelling stage. At the same time, at the swelling stage, solvent molecules quickly penetrate intermolecular spaces, break intermolecular bonds, and, pushing apart the polymer chains, change the polymer structure (Xiong *et al.*, 2018; Kurenkov *et al.*, 2002). In this case, the solvent actively interacts with the active groups of the polymer creating solvated complexes of various structures and volumes. At this time, the surface of the polymer particles at the initial stage of the process plays the role of a semipermeable partition, and the swollen particle acts as an osmotic cell. During swelling, the interface passes through a certain amount of solvent and gradually moves into the substance at a rate equal to the diffusion rate of the solvent (Zinalizadeh *et al.*, 2017; Touze *et al.*, 2015; Matilainen *et al.*, 2005). From the thermodynamic point of view, spontaneous dissolution of HMCs is accompanied by a decrease in the isobaric-isothermal potential according to the well-known equation.

## 2. Methods

### *Determination of the MW of PAA macromolecules*

The viscosity of the solutions was determined viscometrically by a capillary viscometer, and the MW of macromolecules was calculated by the Mark-Houwink equation (Sharma *et al.*, 2006):

$$[\eta] = K \cdot M^\alpha, \quad (1)$$

where  $[\eta]$  is the characteristic viscosity found graphically by standard methods using solutions of different concentrations;

"K" and " $\alpha$ " are constants;

"K" characterizes this type of polymer in a specific solvent;

The value " $\alpha$ " is determined by the shape of macromolecules in solution and additionally characterizes their flexibility.

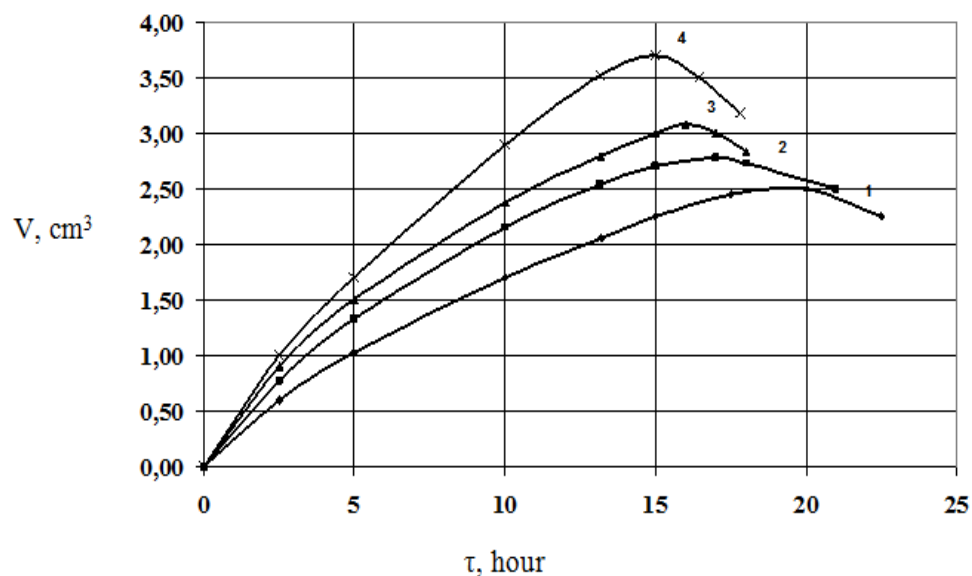
For a water PAA solution, these constants are  $K = 0.63 \cdot 10^{-4}$ ,  $\alpha = 0.8$ .

## 3. Results and Discussion

We propose three options of changing the structure and properties of PAA macromolecules using reagent modification due to the interaction of Magnaflok anionic PAA (M-156) with specially selected components (modifiers) containing two or more functional groups.

**Modification with glycols and chlorohydrins.** We selected chemically active organic modifiers with a small carbon chain belonging to the class of glycols (propylene glycol (PG)) and the class of chlorohydrins (ethylene chlorohydrin (ECH) and propylene chlorohydrin (PCH)). The preparation of PAA solutions from PAA powders included a swelling stage. At the swelling stage, solvent molecules quickly penetrate intermolecular spaces, break intermolecular bonds, and, pushing apart the polymer chains, change the polymer structure (Xiong *et al.*, 2018; Kurenkov *et al.*, 2002). In this case, the solvent actively interacts with the active groups of the polymer creating solvated complexes of various structures and volumes. At this time, the surface of the polymer particles at the initial stage of the process plays the role of a semipermeable partition, and the swollen particle acts as an osmotic cell. During swelling, the interface passes through a certain amount of solvent and gradually moves into the substance at a rate equal to the rate of solvent diffusion (Owen *et al.*, 2002). From the thermodynamic point of view, spontaneous dissolution of HMCs is accompanied by a decrease in the isobaric-isothermal potential  $\Delta G$  according to the well-known equation. During swelling in the presence of water, chemical crosslinking of macromolecules occurs while they gradually detach from the crystalline surface of flocculants during dissolution and go into the solution, i.e. each of the macromolecules carries the modifier molecules fixed on it into the solution. The kinetics of the PAA swelling process in various water systems in the presence of PG, PCH, and ECH has been studied (Fig. 1).

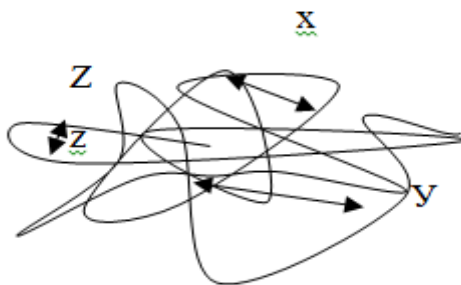
It follows from Figure 1 that the rate of swelling of PAA is the highest for an aqueous system with ECH, in the presence of which the time of transition of the system to the region of unlimited swelling (inflection points on the graphs) was 15 hours instead of 20 hours in the presence of water, i.e. decreased by 5 hours. The following kinetic sequence of the swelling rate for the selected modifiers was obtained:  $V_{ECH} > V_{ech} > V_{pg} > V_{H_2O}$ .



**Fig. 1.** Swelling curves (dependence of the volume of the swollen gel on time) of the initial and modified flocculant M-156: 1: initial flocculant on water; 2, 3, 4: PAA modified by PG, PCH, and ECH, respectively

This behavior of PAA when it swells in the presence of selected modifiers is explained by the behavior of macromolecules and the structure of modifiers. The most active modifiers are chlorohydrins that interact with functional groups of PAA macromolecules during the formation of covalent and hydrogen bonds with PAA. Modification in the presence of PG occurs due to the formation of weaker hydrogen bonds. The faster swelling of the flocculant under the action of ECH is explained by the shorter length of its molecules compared to the length of the PCH molecules.

During swelling, individual sections of the molecular chain are cross-linked, corresponding in size to the lengths of the modifier molecules (Fig. 2).



**Fig. 2.** Scheme of PAA macromolecule crosslinking

At the same time, the conformational structure of polymer macromolecules is more rigidly fixed in space. ECH molecules overlap small loops of the structure (Z), while PG and PCH molecules overlap larger loops (X, Y). After complete dissolution of the PAA sample in an aqueous system by standard methods according to the Flory equation (Kim *et al.*, 2001), important volumetric characteristics of its macromolecules were determined (Table 1).

**Table 1.** Volumetric characteristics of modified flocculants

Flocculant	Modifier	$h \cdot 10^5, \text{cm}$	$m^*$	$F \cdot 10^{12}$	$n^*$	$V_M^\Gamma \cdot 10^{-3}, \text{nm}^3$	$p^*$
M-156	PG	9.5	1.27	3.2	0.8	26.9÷8.6	1.53÷1.48
	ECH	7.8	1.1	3.9	0.88	23.4÷7.4	1.33÷1.29
	PCH	9.0	1.2	3.5	0.98	25.5÷8.1	1.45÷1.41

$h$  is the average statistical distance between the ends of the molecular chain,  $F$  is the flexibility of the macromolecule,  $V_M^\Gamma$  is the hydrodynamic volume occupied by a unit of weight of macromolecules.  $m^* = \frac{h}{h_0}$ ;  $n^* = \frac{\Gamma}{\Gamma_0}$ ;  $p^* = \frac{V_M^\Gamma}{V_{M_0}^\Gamma}$ , where  $h_0, \Gamma_0, V_{M_0}^\Gamma$  are the corresponding values for the initial flocculants prepared on water.

From the data in Table 1 it follows that PAA macromolecules crosslinked with PG are more voluminous than macromolecules crosslinked with ECH and PCH. They have increased the distances between the ends of molecular structures and increased the overall hydrodynamic volume while losing the flexibility of the chain. This fact can be explained by the higher hydrophilicity of PG molecules compared to the reduced hydrophilicity of ECH and PCH molecules.

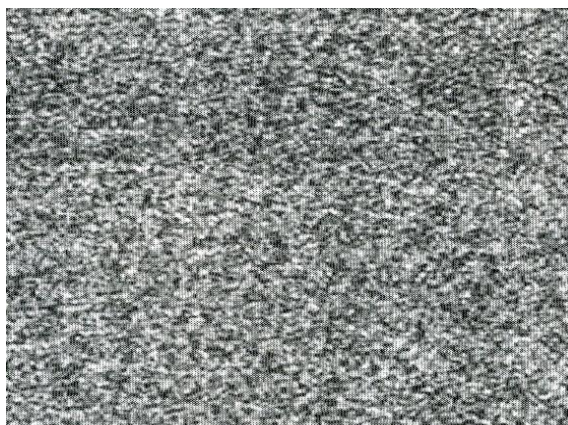
Based on the values of the characteristic viscosity, the  $[\eta]$  MWs of modified and unmodified macromolecules have been found, presented in Table 2.

**Table 2.** MWs of initial and modified anionic flocculants

Modifier	Flocculant	$[\eta]$ , cm <sup>3</sup> /g	MW, million amu
without modifier	M-156	46.9	18.8
PG		73.3	29.3
ECH		49.2	19.8
PG		64.9	25.9

From Table 2 it follows that as a result of crosslinking with the selected modifiers, the MW of the initial polymers increases by 1.4-2.4 times. According to the literature data, such an increase in viscosity, and, accordingly, MW, is due both to the transformation of the globular form of macromolecules into the fibrillar one and due to an increase in the volume of macromolecules during the interaction of polymer chains and modifiers, leading to their crosslinking. The greatest effect is observed when PG is used as a modifier (Mahvi & Razavi, 2005). The mechanism of modification of PAA using PCH occurs due to covalent and hydrogen bonds.

The structure of macromolecules of high-anion flocculant M-156 modified with PG was studied by scanning electron microscopy (Fig. 3).



**Fig. 3.** Electronic photo of flocculant M-156 modified by PG

It follows from Fig. 3 that the perfectly smooth, homogeneous surface of the modified flocculant indicates the formation of highly structured systems. It is assumed that due to the bonds formed, there are no fragments of chains of macromolecules, separate unbound strands of macromolecules, or strands of macromolecules with low MW. The presence of an ordered homogeneous structure additionally experimentally proved the fact that the polymer is sewn into a dense viscous mesh, resistant to ultraviolet (UV) light in daytime conditions, and there is no photo destruction of PAA macromolecules under standard storage conditions with the formation of individual PAA macromolecules.

**Modification by amino acids.** The choice of such modifiers is objective, because according to the well-known practical like-attracts-like chemistry rules, PAA macromolecules, which are a simplified protein model, can enter into chemical

interactions with amino acids. Two amino acids were used as modifiers: a low-molecular-weight nonpolar  $\alpha$ -amino acid (glycine) and a polar  $\alpha$ -amino acid (serine).

Features of modification and characteristics of PAA macromolecules by amino acids are presented in Table 3.

**Table 3.** Volumetric characteristics of modified flocculants

Flocculant	Modifier	$\bar{r} \cdot 10^5, \text{ cm}$	$m^*$	$F \cdot 10^{12}$	*	$V_M^\Gamma \cdot 10^{-3}, \text{ nm}^3$	$p^*$
M-156	Serine	15.5	1.30	2.2	0.81	260.5÷66.70	3.8÷3.4
	Glycine	14.5	1.22	2.2	0.82	234.1÷57.0	3.44÷2.99

Table 3 shows that serine is the most effective modifier among the selected amino acids. The hydrodynamic volume of PAA macromolecules modified with serine is 7-15% higher than the hydrodynamic volume of PAA macromolecules modified with glycine and 2 times higher than the hydrodynamic volume of its macromolecules when modified with PG (Table 1). Serine modification of PAA macromolecules is more effective than modification by other modifiers used.

An option of the mechanism of modification of PAA by serine is proposed: it occurs due to a grid of hydrogen bonds between PAA (N, O) heteroatoms and hydrogen, oxygen, and nitrogen atoms of the modifier functional groups according to the following scheme with the possible formation of two structures.

From the presented structures of the modified complex, it follows that in the process of modification, hydrogen bonds play a major role in the process of structure formation, as well as in the organization of the secondary structure of the protein.

The use of samples of the obtained modified PAA solutions with special rheological properties for wastewater treatment of various compositions has proved to be highly efficient.

### 3. Conclusion

1. The positive effect of the used modifiers (ECH, PCH, and PG) on the rate of swelling and dissolution of PAA powder has been proven. It has been found that the highest swelling rate is observed for the aqueous system in the presence of ECH. A sequence of PAA swelling rates has been obtained in the presence of selected modifiers:  $V_{ECH} > V_{PCH} > V_{pg} > V_{H_2O}$ .

2. Macromolecular characteristics of modified structures in an aqueous medium have been determined. It has been proved that PAA macromolecules modified by PG are more voluminous than macromolecules modified by ECH and PCH and that they have increased distances between the ends of molecular structures with simultaneous loss of chain flexibility.

3. It has been found that the MW of the initial polymers increases by 1.4-2.4 times with reagent modification. The greatest effect of increasing the macromolecular weight is observed when PG is used as a modifier.

4. The mechanism of modification of PAA using PCH based on the action of covalent and hydrogen bonds has been presented. By electron microscopy, the presence of an ordered homogeneous structure in a cross-linked polymer with a dense viscous



mesh has been established.

5. Two amino acids have been used as special modifiers: a low MW nonpolar  $\alpha$ -amino acid (glycine) and a polar  $\alpha$ -amino acid (serine). It has been found that the most effective modifier among the selected amino acids is serine. A comparative analysis of the results of the experiments has proved that the hydrodynamic volume of PAA macromolecules modified with serine is 7-15% higher than the hydrodynamic volume of PAA macromolecules modified with glycine, and 2 times higher than the hydrodynamic volume of its macromolecules when modified with PG. We have proposed an option of the PAA modification mechanism by serine which occurs due to a network of hydrogen bonds between PAA (N, O) heteroatoms and hydrogen, oxygen, and nitrogen atoms.

6. In general, the proposed methods of reagent modification of PAA are promising and create prerequisites for further research in the field of changing and fixing conformational changes of macromolecules of HMCs and their effective use in industrial technologies.

## References

- Baraniak, B., Niezabitowska, M., Pielecki, J., & Wójcik, W. (2004). Evaluation of usefulness of Magnafloc M-22S flocculant in the process of obtaining protein concentrates from peas. *Food Chemistry*, 85(2), 251-257.
- Bolto, B., Gregory, J. (2007). Organic polyelectrolytes in water treatment. *Water Research*, 41(11), 2301-2324.
- Chen, Y., Li, X., Zizeng, W., Feng, L., Xie, J., Lin, Z., ... & Zheng, H. (2021). Research on a new cationic polyacrylamide (CPAM) with a cationic microblock structure and its enhanced effect on sludge condition and dewatering. *Environmental Science and Pollution Research*, 28(37), 51865-51878.
- Dai, X., Luo, F., Zhang, D., Dai, L., Chen, Y., & Dong, B. (2015). Waste-activated sludge fermentation for polyacrylamide biodegradation improved by anaerobic hydrolysis and key microorganisms involved in biological polyacrylamide removal. *Scientific Reports*, 5(1), 1-13.
- Gholami, M., Ghaneyan, M.T., Fatemi, S.S., Talebi, P. & Dalvand, A. (2020). Investigation of the effectiveness of the coagulation and flocculation process in the wastewater treatment of paper and cardboard, *International Journal of Environmental Analytical Chemistry*.
- Joshi, S.J., Abed, R.M.M. (2017). Biodegradation of polyacrylamide and its derivatives. *Environm. Processes*, 4(2), 463-476.
- Karam A., Bahum E.S. and Zaher K. (2021). Coagulation/flocculation process for wastewater treatment of textile factories: experimental and numerical perspectives. *International Journal of Sustainable Engineering*. 14(5), 983-995.  
<https://doi.org/10.1080/19397038.2020.1842547>.
- Kim, J.S., Akeprathumchai, S., & Wickramasinghe, S.R. (2001). Flocculation to enhance microfiltration. *Journal of Membrane Science*, 182(1-2), 161-172.
- Kitahara, Y., Okuyama, K., Ozawa, K., Suga, T., Takahashi, S., & Fujii, T. (2012). Thermal decomposition of acrylamide from polyacrylamide: time-resolved pyrolysis with ion-attachment mass spectrometry. *Journal of Thermal Analysis and Calorimetry*, 110(1), 423-429.
- Kurenkov, V.F., Khartan, H.G. & Lobanov, F.I. (2002). Degradation of polyacrylamide and its derivatives in acal solutions. *Russ J. Appl. Chem.* 75(7), 1039-1050.  
<http://dx.doi.org/10.1023/A:1020747523268>

- Liu, Y., Ma, J., Lian, L., Wang, X., Zhang, H., Gao, W., & Lou, D. (2021). Flocculation performance of alginate grafted polysilicate aluminum calcium in drinking water treatment. *Process Safety and Environmental Protection*, 155, 287-294.
- Mahvi, A.H., Razavi, M. (2005). *Application of polyelectrolyte in turbidity removal from surface water*. Science Publications.
- Mao, S., Xu, X., Zhang, L., Bai, B., Hu, N., & Wang, H. (2021). Methylated mud snail protein as a bio-flocculant for high turbidity wastewater treatment. *Water Science and Technology*, 84(3), 737-751.
- Matilainen, A., Lindqvist, N., & Tuhkanen, T. (2005). Comparison of the efficiency of aluminium and ferric sulphate in the removal of natural organic matter during drinking water treatment process. *Environmental Technology*, 26(8), 867-876.
- Naruka, A.K., Suganya, S., Kumar, P.S., Amit, C., Ankita, K., Bhatt, D., & Kumar, M.A. (2021). Kinetic modelling of high turbid water flocculation using native and surface functionalized coagulants prepared from shed-leaves of *Avicennia marina* plants. *Chemosphere*, 272, 129894.
- Owen, A.T., Fawell, P.D., Swift, J.D., & Farrow, J.B. (2002). The impact of polyacrylamide flocculant solution age on flocculation performance. *International Journal of Mineral Processing*, 67(1-4), 123-144.
- Sharma, B.R., Dhuldhoya, N.C., & Merchant, U.C. (2006). Flocculants-an ecofriendly approach. *Journal of Polymers and the Environment*, 14(2), 195-202.
- Shevchenko, T.V. (2004). Applied colloidal chemistry. Flocculants and flocculation. *Kemerovo: Kemerovo Technological Institute of Food Industry*.
- Touzé, S., Guerin, V., Guezennec, A.G., Binet, S., & Togola, A. (2015). Dissemination of acrylamide monomer from polyacrylamide-based flocculant use—sand and gravel quarry case study. *Environmental Science and Pollution Research*, 22(9), 6423-6430.
- Ustinova, Yu.V., Temirev, A.Yu., Shevchenko, T.V. & Ulrich, E.V. (2008). The use of modified and unmodified flocculants for wastewater treatment of dairy industry. *Fundamental Research*, 6, 70-71.
- Wang, D., Liu, X., Zeng, G., Zhao, J., Liu, Y., Wang, Q., ... & Yang, Q. (2018). Understanding the impact of cationic polyacrylamide on anaerobic digestion of waste activated sludge. *Water Research*, 130, 281-290.
- Xiong, B., Loss, R.D., Shields, D., Pawlik, T., Hochreiter, R., Zydney, A.L., & Kumar, M. (2018). Polyacrylamide degradation and its implications in environmental systems. *NPJ Clean Water*, 1, 17.
- Yu, Y., Sun, Y., Zhou, J., Chen, A., & Shah, K. J. (2021). Preparation and characterization of high-efficiency magnetic heavy metal capture flocculants. *Water*, 13(13), 1732.
- Zinatizadeh, A.A., Ibrahim, S., Aghamohammadi, N., Mohamed, A.R., Zangeneh, H., & Mohammadi, P. (2017). Polyacrylamide-induced coagulation process removing suspended solids from palm oil mill effluent. *Separation Science and Technology*, 52(3), 520-527.