

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

<https://doi.org/10.32014/2019.2518-1491.17>

Volume 2, Number 434 (2019), 44 – 49

UDK 541.18

N.O. Dzhakipbekova¹, L.S. Eshenko², A.N. Isayeva¹, E.O. Dzhakipbekov¹, A.B. Issa¹,

¹ South Kazakhstan State University, Shymkent, Kazakhstan;

² Belarusian State Technical University, Belarus

dzhakipbekova@mail.ru, eshenko@mail.ru, isaeva.aika@mail.ru*,

erjan1577@mail.ru, isa.aziza@mail.ru

PHYSICAL-CHEMICAL AND COLLOID-MECHANICAL METHODS OF RESEARCH OF MODIFIED POLYMER REAGENTS OF THE M-PAA SERIES AND THEIR APPLICATION FOR OBTAINING OF OINTMENT

Abstract. This article discusses the surface, bulk and structural properties of polymers. It was determined that the limit value σ for M-PAA (MEA) and M-PAA (PV) is established faster than for individual solutions. It has been established that in polymers viscosity and electrical conductivity increase with increasing concentration, i.e. M-PAA (MEA) and M-PAA (PV) are polyfunctional polyelectrolytes, polymers M-PAA (MEA) and M-PAA (PV) are thermostable. For the study a complex of physicochemical methods were used: potentiometry, spectroturbidimetry, conductometry, viscometry, IR spectroscopy, elemental analysis, thermogravimetry, measurement of surface tension by the Wilhelm method.

Key words: modified polymers, M-PAA (MEA), M-PAA (PV), IR spectra, thermal stability.

Introduction

The preparation of new polymer reagents from their synthesis in the laboratory to their industrial production as an ointment is relatively long and expensive process. Therefore, the most promising and justified way is to expand the range of polymer reagents by modifying the already known base samples [1]. In the [2] work authors synthesized a serial of amino-modified PAN fibers by the reaction of PAN fiber with TETA in the presence of water. The weight and alkali content, namely, amino grafting degree, would be improved by prolonging reaction time and increasing reaction temperature.

2 Experimental part

2.1 Preparation of solutions

For deposition, a 1% polymer solution and a 0.15% hydrochloric acid solution were prepared. With constant stirring, a solution of hydrochloric acid was added to a 1% polymer solution; as a result, the pH dropped to 4 and a gel-like polymer precipitated out, which was washed 3 times with water. Dioxane was precipitated. In this case, the remnants of the starting products were dissolved in dioxane, and the polymer precipitated in the form of a gel. The precipitated, washed samples were dried in a vacuum desiccator. Dialysis of a 1% polymer solution was carried out in a celluloid packet, periodically changing the water (within 1-2 days). Next, the precipitated dialyzed samples were dried in a vacuum oven $T = 40-450\text{ }^{\circ}\text{C}$ for 8-10 hours. To determine the composition of the polymers, thermal analyzes were performed.

2.2 Research Methods

IR spectroscopy and electron microscopy analyzes.

The IR spectra of polymers were interpreted according to the guidelines [3]. The analysis was carried out on an IR-20 spectrometer (in vaseline oil in the range of $700-4000\text{ m}^{-1}$).

Device: FTIR-spectrometer Shimadzu IR Prestige-21 with prefixed disturbed total internal reflection (ATR) Miracle from Pike Technologies.

Thermogravimetric studies of the polymers were carried out on a derivatogaf in an atmosphere of air at a rate of temperature rise up to 450 °C per minute, and a sample weight of 150 mg.

For a quantitative comparison of the thermal stability of the polymers under study, the activation energies of destruction were calculated [4].

The viscosity of solutions of polyelectrolytes was measured in a viscometer of the Ubbelohde type [5], with a hanging level. For viscometric studies, re-precipitated and thoroughly dried polymers were used.

The viscometer was placed in a thermostat, the temperature was maintained with an accuracy of ± 0.01 °C.

The concentration of the solution after dilution was calculated by the formula:

$$C = \frac{gV_i - 100}{V(V_i + V_j)} P_i / P_2 = \frac{ciV_i}{V_i + V_j}, \quad (1)$$

where g is the polymer weight, g;

V is the volume of the volumetric flask, ml;

V_i is the volume of the solution filled in viscometers, ml;

V_j is the volume of the added solvent, ml;

P_i / P_j is the solvent density ratio.

The calculation of the relative $\eta_{rel.}$ (rel.) Specific $\eta_{spec.}$ (spec), The reduced $\eta_{red.}$ (red.) Viscosities was carried out according to the following formulas:

$$\eta_{rel.} = \frac{\tau_i}{\tau_0}; \quad (2)$$

$$\eta_{spec.} = \eta_{rel.}^{-1}; \quad (3)$$

$$\eta_{red.} = \frac{\eta_{spec.}}{c} \quad (4)$$

The characteristic viscosity (η) was found from the graphical dependence $\eta_{red.}$ (C) by extrapolating the straight lines to zero polymer concentration [6].

Measurement of the surface tension was carried out according to the method of Wilhelmy.

When determining the surface tension of the solutions by the method of Wilhelmi, the immersion force of the plates in the liquid was continuously measured. The magnitude of this force depends on the wetting of the measuring plate with liquid.

In the present work, a polished glass plate was used as a measuring plate, as well as made from a plate.

The calculation was carried out as follows:

$$\sigma = \frac{p+shd}{2(1+b)}, \quad (5)$$

p -weight plate, g; s - cross-sectional area, cm; l is the width of the plate, cm; $-b$ is plate thickness (-), cm; h -immersion depth, cm; d -density of the measured liquid, g / cm; g -acceleration of gravity.

The surface tension was measured with a thermostatically controlled glass cell with a lid at a temperature of 25 °C; the temperature was kept constant using an I-2 ultra thermostat with an accuracy of ± 0.02 . The reading of the values of P_x was carried out using toroidal weights of the type VT-500 with an accuracy of ± 1 mg.

The pH of polymer solutions was measured on a pH-340 potentiometer with an accuracy of ± 0.05 . The pH in a thermostatically controlled cell, in which the temperature was maintained with an accuracy of ± 0.01 . Further, the formula determined the conductivity (χ):

$$\chi = \frac{\alpha}{Rx}; \quad (6)$$

where α is the cell constant: $\alpha = 0.000147\text{m}\cdot\text{cm}^{-1}$, at $T = 250$

Turbidity was determined on a calorimeter of the type FEK-56 with $\alpha = 434\text{nm}$. Solutions of the corresponding fractions of polymers were used as reference solutions.

3 Results and discussions

The study of the structural properties of the polymers M-PAA (MEA), M-PAA (PV).

The IR spectra of polymers, whose interpretation was carried out according to the guidelines [7], contain absorption bands in the range of $3200\text{--}3500\text{ cm}^{-1}$, which can be attributed to hydroxyl groups of an alcoholic nature, both free and hydrogen bonded. Bands with frequencies of $1405\text{--}1410$ and also $1610\text{--}1630\text{ cm}^{-1}$ characterize the presence of $-\text{NO}_2$, $-\text{COO}^-$ groups. According to some authors [8], the pictogroup included in the core contributes to the stability of the first to destruction.

Absorption bands in the range of $1600\text{--}1630\text{ cm}^{-1}$ can be attributed to skeletal vibrations of $-\text{C}=\text{C}$ bonds, rather distinct bands of stretching vibrations — CH^2 groups are observed in the short-wave part of the spectra ($2940\text{--}2970\text{ cm}^{-1}$). Characteristic for $-\text{CH}$ groups are peaks at frequencies of $780\text{--}790\text{ cm}^{-1}$, and a maximum at a frequency of 1370 cm^{-1} can be attributed to deformational vibrations of $-\text{CH}$ groups. In the spectrum of the studied samples, new bands are noted at frequencies of 1480 and 1690 cm^{-1} , which can be identified as $-\text{COONH}_2$ and $-(\text{CO})_2\text{NH}$ (Figure 1-5) [9].

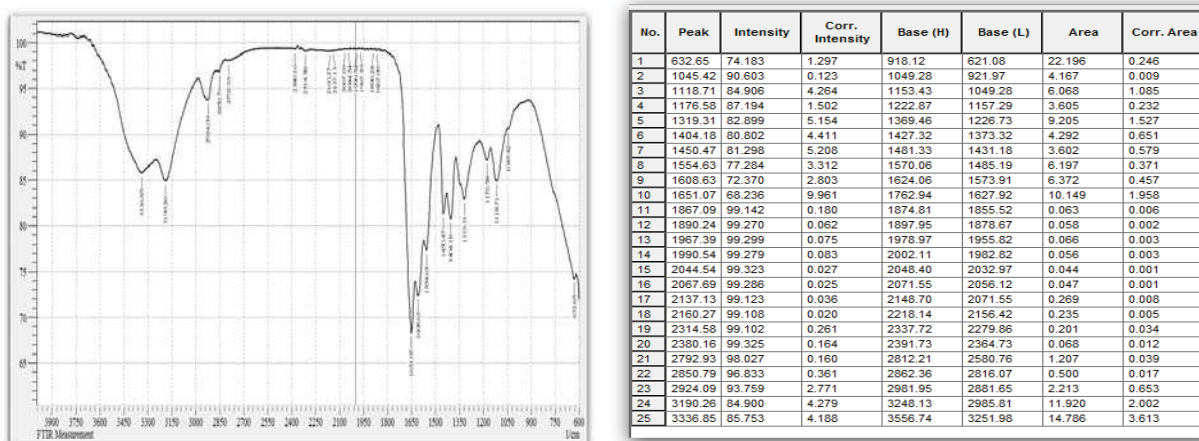


Figure 1 - The main polymer PAA (Polyacrylamide) powder

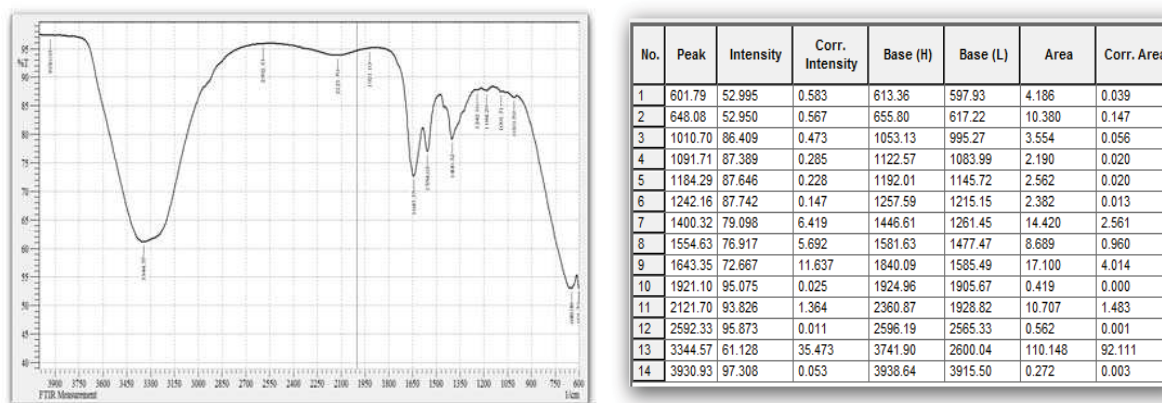


Figure 2 - MEA-PAA 1, colorless, viscous, non-flowing solution

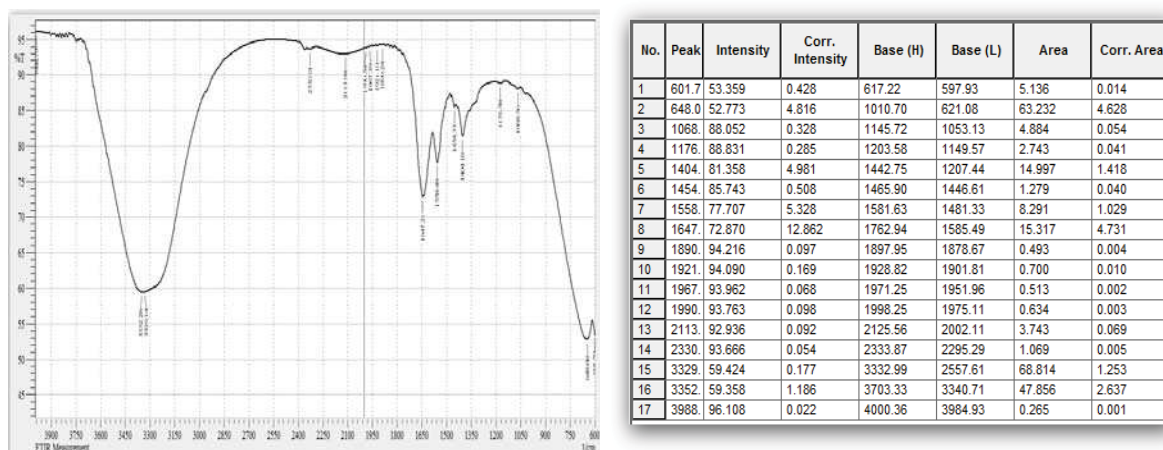
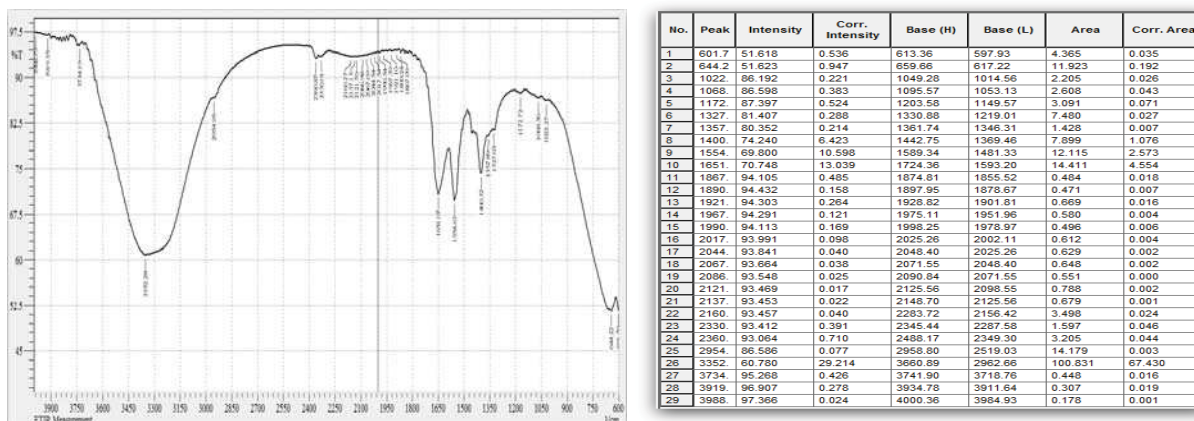
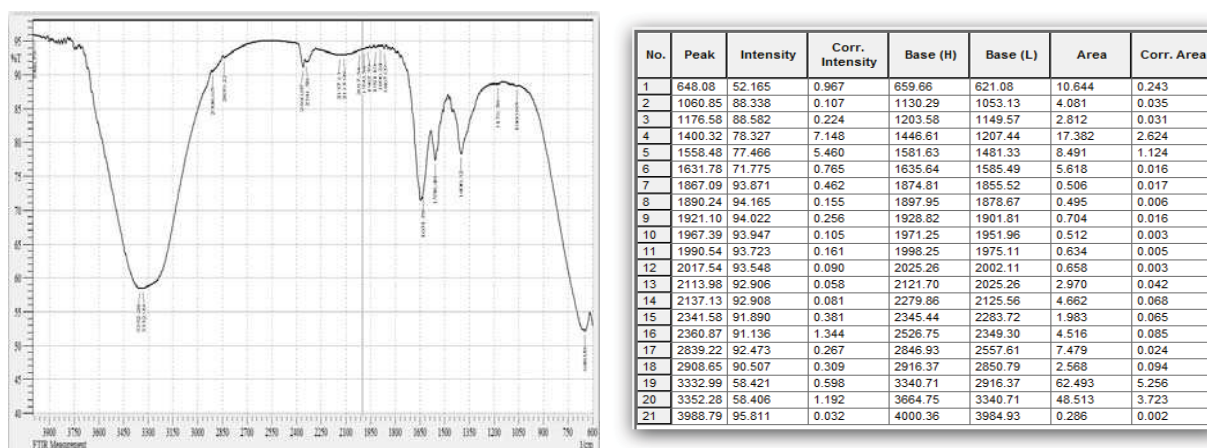


Figure 3 - MEA-PAA 2, yellowish, viscous, non-flowing solution

Figure 4 - PAA-H₂O₂, colorless, viscous, weakly flowing solutionFigure 5 - PAA-H₂O₂, yellowish, viscous, non-flowing solution

Thus, the IR spectra of the studied samples contain: $-NO_2$, $-COOH$, $-(CO)_2NH$, $-CONH_2$, $-OH$ groups.

The stability of the obtained polymer to thermo-oxidative degradation was studied on a derivatograph of the Paulik-Paulik-Erdey system using the method of “dynamical thermogravimetry”. The heating rate is 6 deg/min., The interval is 293-870 K. (Table 1).

Table 1 - Characteristics of thermal stability of polymers M-PAA (MEA), M-PAA (PV), K-9

Polymer	T	E, kJ/ mol	Weight loss	Initial weight, kg·10 ⁻¹
M-PAA (MEA)	698,4	96,2	31,5	552,6
K-9	670,7	78,7	49,8	552,3
M-PAA (PV)	703,4	94,3	39,4	550,8

From the data in the table it can be seen that the weight loss in thermogravimetry K-9 is 48.3%, and the polymer M-PAA (MEA) obtained on its basis is 30%, which is 1.5 times less. The weight loss of the polymer M-PAA compared with K-9 is also lower. In addition, the temperature of the onset of active decomposition in new samples increases markedly compared with the baseline ones. Thus, a qualitative assessment of the thermal stability of the process is obtained.

A quantitative comparison of the thermal stability of the samples under study will allow the calculation of the activation energy of destruction [3].

So, for thermo-oxidative destruction of K-9, 78.5 kJ / mol is required, while for the destruction of the polymer M-PAA (PV) - 85.3 kJ / mol, polymer M-PAA (MEA) - 84.1 kJ / mole. This gives grounds to attribute them to thermostable polymers [7].

Conclusion. Summarizing the above, we can draw the following conclusions:

a) Surface properties:

- The limiting value of σ for M-PAA (MEA) and M-PAA (PV) is established faster than for individual solutions;

- adsorption in these polymers is mainly determined by the diffusion of the macromolecule;

c) Bulk properties:

- in the polymers, with increasing concentration, viscosity and electrical conductivity increases, i.e. M-PAA (MEA) and M-PAA (PV) are polyfunctional polyelectrolytes.

c) Structural properties:

- polymers M-PAA (MEA) and M-PAA (PV) are thermostable;

- IR spectra of samples contain $-NO_2$, $-COOH$, $-CN$, $-SO_3Na$, $-OH$,

$-CONH_2$ groups.

ӨОК 541.18

Н.О. Джакипбекова¹, Л.С. Ещенко², А.Н. Исаева¹, Е.О. Джакипбеков¹, А.Б. Иса¹

¹ М.Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті, Шымкент, Қазақстан;

² Белорусия мемлекеттік техникалық университеті, Белорусия

М-РАА СЕРИЯЛЫ МОДИФИЦИРЛЕНГЕН ПОЛИМЕРЛІ РЕАГЕНТТЕРДІҢ ФИЗИКА-ХИМИЯЛЫҚ ЖӘНЕ КОЛЛОИДТЫ-МЕХАНИКАЛЫҚ ӘДІСТЕРМЕН ЗЕРТТЕУ ЖӘНЕ ОЛАРДЫ МАЗЬДЕРДІ АЛУДА ҚОЛДАНУ

Аннотация. Бұл мақалада полимерлердің беттік, көлемдік және құрылымдық қасиеттері қарастырылады. М-РАА (МЕА) және М-РАА (PV) шекті мәні жеке ерітінділерге қарағанда тезірек орнығатыны анықталды. Концентрацияларының артуына байланысты полимерлердің тұтқырлығы мен электрөткізгіштігі артатыны анықталды, яғни М-РАА (МЕА) и М-РАА (PV) полифункционалды полиэлектролиттер болып табылады, М-РАА (МЕА) и М-РАА (PV) полимерлері термостабильді болып табылады. Зерттеу үшін физика-химиялық әдістер жиынтығы пайдаланылды: потенциометрия, спектротурбидиметрия, кондуктометрия, вискозиметрия, ИК-спектроскопия, элементтік анализ, термогравиметрия, Вильгельми әдісімен беттік керілуді өлшеу.

Түйін сөздер: модифицирленген полимерлер, М-РАА (МЕА), М-РАА (PV), ИК спектрлері, жылу тұрақтылығы

Н.О. Джакипбекова¹, Л.С. Ещенко², А.Н. Исаева¹, Е.О. Джакипбеков¹, А.Б. Иса¹

¹ Южно-Казахстанский государственный университет, Шымкент, Казахстан

² Белорусский государственный технический университет, Белорусия

ФИЗИКО-ХИМИЧЕСКИЕ И КОЛЛОИДНО-МЕХАНИЧЕСКИЕ МЕТОДЫ ИССЛЕДОВАНИЯ МОДИФИЦИРОВАННЫХ ПОЛИМЕРНЫХ РЕАГЕНТОВ СЕРИИ М-РАА И ИХ ПРИМЕНЕНИЕ ДЛЯ ПОЛУЧЕНИЯ МАЗЕЙ

Аннотация. В данной статье рассматриваются поверхностные, объемные и структурные свойства полимеров. Было определено, что предельное значение σ для М-РАА (МЕА) и М-РАА (РВ) устанавливается быстрее, чем для отдельных растворов. Установлено, что в полимерах вязкость и электропроводность увеличиваются с увеличением концентрации, то есть М-РАА (МЕА) и М-РАА (РВ) являются полифункциональными полиэлектролитами, полимеры М-РАА (МЕА) и М-РАА (РВ) являются термостабильными. Для исследования использовали комплекс физико-химических методов: потенциометрия, спектротурбидиметрия, кондуктометрия, вискозиметрия, ИК-спектроскопия, элементный анализ, термогравиметрия, измерение поверхностного натяжения методом Вильгельми.

Ключевые слова: модифицированные полимеры, М-РАА (МЕА), М-РАА (РВ), ИК-спектры, термостабильность.

Information about authors:

Dzhakipbekova N.O. - Doctor of Technical Sciences, professor, M. Auezov SKSU, Kazakhstan, Shymkent, Tauke Khan 5 st., tel. : +7 (701) 292 370 E-mail: dzhakipbekova@mail.ru, <https://orcid.org/0000-0003-3496-1910>;

Yeshchenko L.S.- Doctor of Technical Sciences, professor, Belarusian State Technical University, tel: + 7 (702) 254 3362 E-mail: eshenko@mail.ru, <https://orcid.org/0000-0003-4712-9883>;

Isaeva A.N.- PhD student of M. Auezov SKSU, Kazakhstan, Shymkent, Tauke Khan 5 st., tel. : +7 (7753) 571 214 E-mail: isaeva.aika@mail.ru, <https://orcid.org/0000-0002-4833-1904>

Dzhakipbekov E.O. – PhD student of M. Auezov SKSU, Kazakhstan, Shymkent, Tauke Khan 5 st., E-mail: erjan1577@mail.ru, <https://orcid.org/0000-0002-8021-816X>;

Issa A.B. - PhD student of M. Auezov SKSU, Kazakhstan, Shymkent, Tauke Khan 5 st., tel.: 8775 446 48 67 E-mail: isa.aziza@mail.ru, <https://orcid.org/0000-0002-1508-402X>

REFERENCES

[1] Dzhakipbekova N., Sakibayeva S., Dzhakipbekov E., Ahmet D., Rzabay S., Issa A., Kydryalyeva A., Amantayev E. (2018) The Study of Physical and Chemical Properties of the Water-Soluble Polymer Reagents and their Application as an Ointment. *Oriental Journal of Chemistry*, 34(4):1779-1786.

[2] [Wenbo Zhao](#), [Biao Liu](#) and [Jian Chen](#) (2014) Preparation of Amino-Modified PAN Fibers with Triethylenetetramine as Aminating Reagents and Their Application in Adsorption. *Journal of Nanomaterials*, Volume 2014, Article ID 940908.

[3] Nakanisi K. (1965) *Infrared spectra and the structure of organic compounds*. Moscow. Mir.

[4] Rogovina Z.A., Zubova V.P. (1968) *New in polymer research methods*. Moscow. Mir, p. 148.

[5] Nurakhmetova Zh.A., Kurbashev E. P., Selenova B.S., Borke T., Aseyev V.O., Kudaibergenov S.E. (2019) Synthesis and characterization of carboxymethylated cornstarch. *News of the Academy of sciences of the Republic of Kazakhstan. Series chemistry and technology*. Volume 1, Number 433 (2019), PP.6 – 15, <https://doi.org/10.32014/2019.2518-1491.1>, ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

[6] Newman S., Krigbraum W., Jangier C., Flory R.J., (1954) *Pol Sci*, 14,451.

[7] Shur A.M. (1971) *High Molecular Compounds*. Moscow. High school, p.71.

[8] A.S. 675864 (1980) A method of producing a reagent by calculating for treating clay solutions. - N12. p.71.

[9] Paus K.F. (1957) *Drilling production fluids*. Moscow. Nedra.

Publication Ethics and Publication Malpractice in the journals of the National Academy of Sciences of the Republic of Kazakhstan

For information on Ethics in publishing and Ethical guidelines for journal publication see <http://www.elsevier.com/publishingethics> and <http://www.elsevier.com/journal-authors/ethics>.

Submission of an article to the National Academy of Sciences of the Republic of Kazakhstan implies that the described work has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis or as an electronic preprint, see <http://www.elsevier.com/postingpolicy>), that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder. In particular, translations into English of papers already published in another language are not accepted.

No other forms of scientific misconduct are allowed, such as plagiarism, falsification, fraudulent data, incorrect interpretation of other works, incorrect citations, etc. The National Academy of Sciences of the Republic of Kazakhstan follows the Code of Conduct of the Committee on Publication Ethics (COPE), and follows the COPE Flowcharts for Resolving Cases of Suspected Misconduct (http://publicationethics.org/files/u2/New_Code.pdf). To verify originality, your article may be checked by the Cross Check originality detection service <http://www.elsevier.com/editors/plagdetect>.

The authors are obliged to participate in peer review process and be ready to provide corrections, clarifications, retractions and apologies when needed. All authors of a paper should have significantly contributed to the research.

The reviewers should provide objective judgments and should point out relevant published works which are not yet cited. Reviewed articles should be treated confidentially. The reviewers will be chosen in such a way that there is no conflict of interests with respect to the research, the authors and/or the research funders.

The editors have complete responsibility and authority to reject or accept a paper, and they will only accept a paper when reasonably certain. They will preserve anonymity of reviewers and promote publication of corrections, clarifications, retractions and apologies when needed. The acceptance of a paper automatically implies the copyright transfer to the National Academy of Sciences of the Republic of Kazakhstan.

The Editorial Board of the National Academy of Sciences of the Republic of Kazakhstan will monitor and safeguard publishing ethics.

Правила оформления статьи для публикации
в журнале смотреть на сайте:

www.nauka-nanrk.kz

<http://chemistry-technology.kz/index.php/en/arhiv>

ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

Редакторы: *М. С. Ахметова, Т. А. Апендиев, Аленов Д. С.*
Верстка на компьютере *А. М. Кульгинбаевой*

Подписано в печать 04.04.2019.

Формат 60x881/8. Бумага офсетная. Печать – ризограф.
4 п.л. Тираж 300. Заказ 2.