

ХИМИЯ ПОЛИМЕРОВ

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SYNTHESIS OF POLYACRYLAMIDE HYDROGELS WITH RESCRIPTION PROPERTIES BY THE METHOD OF FRONTAL POLYMERIZATION

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In the last few decades polyacrylamide hydrogels (PAH) are one of the most relevant and sought-after research topics in a variety of scientific disciplines: chemistry, physics, biology, medicine, etc. PAHs are cross-linked polymeric structures capable of swelling and shrinking by absorbing and releasing a large amount of moisture without degradation of the original form. Due to these properties PAHs are necessary in agriculture, bioengineering, pharmacology, medicine, cosmetology, plastic surgery, design of general hygiene products, including diapers, etc.

The presented work is devoted to the study of the kinetics and macrokinetics of the synthesis of PAGs by the frontal polymerization method with the possibility of obtaining a product with prescribed properties. The work shows that the proposed method enables to control the process and, accordingly, provides the properties of the resulting PAHs according to the prescribed requirements of the absorption and release of water (from 0,2 g to 5000 g of water per 1 g of dry hydrogel), and the required physical and mechanical properties – elasticity, mechanical elasticity, ability to withstand high mechanical loads without crumbling.

We note in particular that in contrast to the currently traditional methods of PAH synthesis the proposed method provides the absolute ecological product safety completely free of even traces of residual poisonous monomer – acrylamide.

Figs. 10, references 32.

Introduction

It is known that in the last few decades polymer hydrogels have been of great interest for the international scientific community in relation to their broad range of possibilities of application in various fields of national

economy. It should be noted that there is a large number of academic literature on the subject of synthesis and study of the properties of PAHs [1].

Hydrogels can be obtained on the basis of various polymers and copolymers with different additives, including nanosized, in order to control the absorption and release of water and active substances in accordance with the required physico-mechanical properties [2].

From the data available to date it can be concluded that PAHs have better properties compared to others, both in their absorbability and release of water and active substances, and in the required physico-mechanical properties [3].

As already noted PAHs are traditionally obtained in two stages (Figure 1) - the synthesis of linear polyacrylamide and further cross-linking of the linear macromolecules to form a three-dimensional cross-linked structure of polyacrylamide.

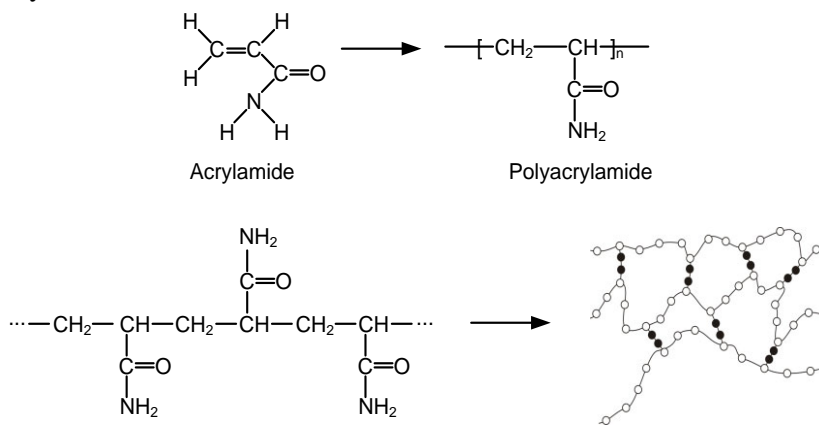


Fig. 1. Two-stage scheme of hydrogel synthesis.

Apart from the traditional methods, it is natural to search for more accessible and economic methods for PAH synthesis. At present, an unconventional method for polymer synthesis, termed frontal polymerization (FP), is of particular interest in many countries. The method was established in the early 70s of the last century on the basis of the studies in the field of adiabatic polymerization in combination with autowave processes, in Russia, Akademgorod, Chernogolovka; there it was virtually exclusively studied until 1991 [4-20], and only after then FP started to spread in USA, followed by many other countries of the world [21].

From numerous countries many scientists were involved in the study on the patterns of synthesis of various hydrogels, in particular, PAHs by the method of FP due to its high cost- and energy-effectiveness and environmental soundness [22-30]. Comparing to the traditional methods of hydrogel synthesis, FP really proved to be more advantageous, at least due to the fact that it proceeds in one phase, much faster and yields better results.

The process is more economically advantageous, the process is more profitable, since it proceeds through the release of the heat.

It has been shown that besides the technological profits of the process proceeding in one phase, the method is more economically advantageous because it takes place due to the heat released as a result of the exothermic polymerization, and does not need additional heat supply from outside. Furthermore, FP is easy in implementation and, more importantly, hydrogels obtained by this method, are better in their performance than those obtained by the traditional methods.

However, here it is important to focus on a crucial detail inherent in FP which is practically necessary, and the violation of which may lead to significant problems. The fact is that unlike the traditional methods of polymerization, the specificity of FP consists in the implementation of the process not throughout the entire volume, but lengthwise the reaction ampoule by the mechanism of autowave propagation of a process from one end to the other [24-30]. And this specificity dictates the necessary conditions for each particular case of polymerization, and therefore, thorough theoretical and experimental studies on the implementation of the process are necessary, taking into account all the kinetic and macrokinetic parameters accompanying the process. Since during FP the establishment of a sustained (stable) stationary wave propagation occurs in the direction of wave propagation (along the reaction ampoule) autowave propagation transitions from one condition to another may occur depending on the effects of various kinetic and macrokinetic factors. As a result, such a change in wave nature before the establishment of the optimal propagation rate affects the properties of the resulting product.

The purpose of this work was to study the possibilities of synthesis of PAHs with prescribed properties by the method of FP, along with the possibilities of their regulation according to the requirements of the product.

Experimental section

The experiments on the study of the kinetics of non-isothermal adiabatic polymerization were carried out in an adiabatic calorimeter; the results were compared with the temperature profiles of a process occurring in an autowave propagation mode by the known method of FP [31]. The process was carried out by initiating the front from top to bottom along the reaction ampoule. Reagents: acrylamide (AAM), sodium acrylate (Na acrylate), potassium persulfate, *N,N'*-methylenebisacrylamide purchased from Aldrich, local bentonite. The front velocity was measured along the direction of the reaction process by means of a thermocouple inserted in the recess holes on the glass reaction ampoule. The physico-mechanical properties of the

products were analyzed by Direvatograph Q-1500D, Roman spectroscopy and gel-chromatography.

Results and discussion

As it was mentioned above, during FP a front velocity change is possible, which dramatically affects the product properties. Hence, there is a need to maintain the process' steady modes – the stationarity of the reaction front over the entire cycle of the ongoing process. Failure to incorporate the specified factors may lead to non-reproducibility of the product properties, and make it impossible to synthesize hydrogels with prescribed properties.

In Fig. 2 the temperature profiles of acrylamide, sodium acrylate and initiator- potassium persulfate FP are presented.

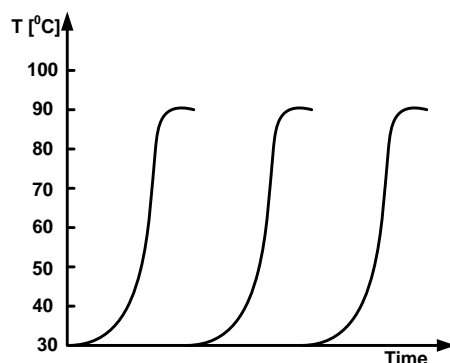


Fig. 2. Temperature profiles of stationary FP (AAM, Na acrylate, potassium persulfate).

As seen in Fig. 2, the temperature profiles are unchanged both in space and time, which indicates a stationary front which, in turn, ensures the homogeneity of hydrogel properties, $T_{\text{lim}}=93\text{ }^{\circ}\text{C}$ (the temperature limit of heating).

In this respect, it must be noted that the establishment of the stationarity occurs after a certain period of time after initiating the front. If, when taking samples for physico-mechanical analysis, the primary part of the gel is not removed the properties of the product will be distorted due to its addition to the total mass. Below is the scheme of the establishment of stationarity in the synthesis of PAHs, which represents the temperature change profiles and the degrees of conversion in the direction of the polymerization front. As shown, the stationarity is established in 2-3 cm, along the length of the reaction ampoule.

Naturally, in the layers adjacent to the beginning of the ampoule the heating occurs on account of an external source of heat that leads to an unsteady polymerization in these layers. As the reaction proceeds, heat is released that is further transferred to the neighboring layers where polymerization process is initiated, and thus, at a distance of 2-3 cm from the beginning of the reaction ampoule the external source no longer plays a

significant role in the ongoing process. Hereinforth, the propagation of the polymerization front takes places on account of the exothermicity of the polymerization reaction, and a stationary condition is established.

In stationary conditions the degree of conversion, the temperature of maximal heating and the velocity of the front remain unchanged along the entire length of the reaction ampoule.

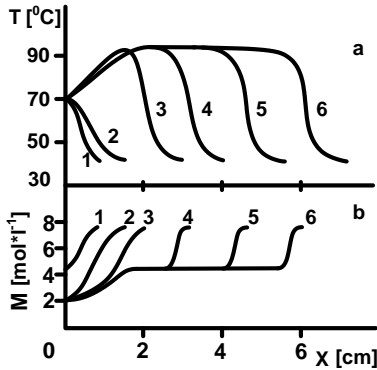


Fig. 3. Profiles of (a) temperature and (b) concentration changes of FP in the direction of the reaction front.

It is clear that the properties of the product will differ depending on the zone from which the samples are taken, and if the product is analyzed as a single whole the results will not correspond to reality, and from experiment to experiment with the same kinetic and macrokinetic conditions the results will be non-reproducible.

In the light of foregoing the following study was made in order to prevent non-reproducibility of data on the gel properties. Fig. 4 shows the kinetic curves of the absorption and release of water for the gel segments from the same sample in different zones of the reaction ampoule.

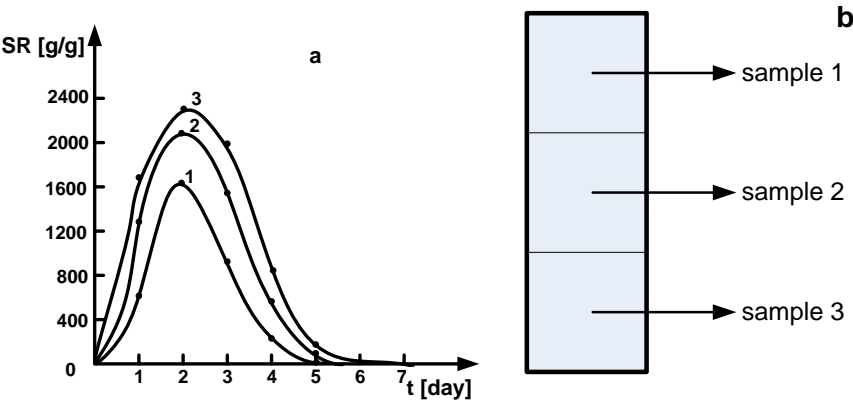


Fig. 4. Kinetic curves of the absorption and release of water for the gel segments from the same sample of PAH (b).

The study of the kinetics of the absorption and release of water of the obtained hydrogels was carried out in light of the above, i.e. the samples were taken only from the zone where FP proceeded in a stationary mode.

PAHs with different concentration ratios of monomers (AAm, Na acrylate) were synthesized by FP. The concentration ratios of AAm and Na acrylate were varied within the following intervals: AAm:Na acrylate = 1:2.5; 2.5:1; 1.75:1.75. The results are demonstrated in Fig. 5.

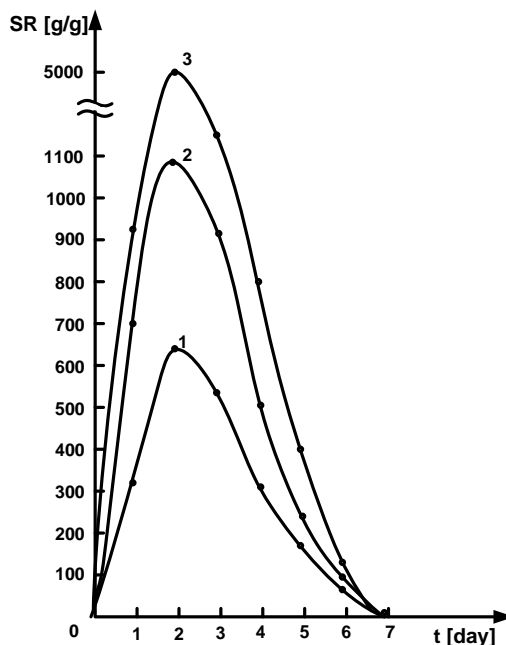


Fig. 5. Kinetic curves of water absorption and release capacity of PAHs with the following concentration ratios of the monomers: AAm:Na acrylate = 1:2.5 (curve 1), AAm:Na acrylate = 2.5:1 (curve 2), AAm: Na acrylate = 1.75:1.75 (curve 3).

As can be seen from the curves of Fig. 5, the maximum absorption of water by the hydrogels is observed at the ratio of AAm:Na acrylate = 1.75:1.75, accounting for 5000 g of water per 1 g of PAH.

In order to obtain PAHs with prescribed properties, including gels with very low absorbability and a long-term release of water and active substances, PAHs with nano additives were synthesized by FP. A colloidal solution of bentonite was used as nano additive. The synthesis of bentonite-containing PAHs (BPAHs) was carried out as follows. 1, 3, 5, 7, and 10 wt% of colloidal solutions of bentonite, which were added to the initial solution of the monomers (AAm, Na acrylate, water and initiator) were prepared in advance, and FP was performed. The temperature profiles of BPAHs FP are similar to those of PAHs, with the only difference that their limiting temperature of heating is lower and amounts to $T_{lim.}=83^{\circ}\text{C}$.

The kinetics of water absorption and release capacity of the synthesized BPAHs was investigated.

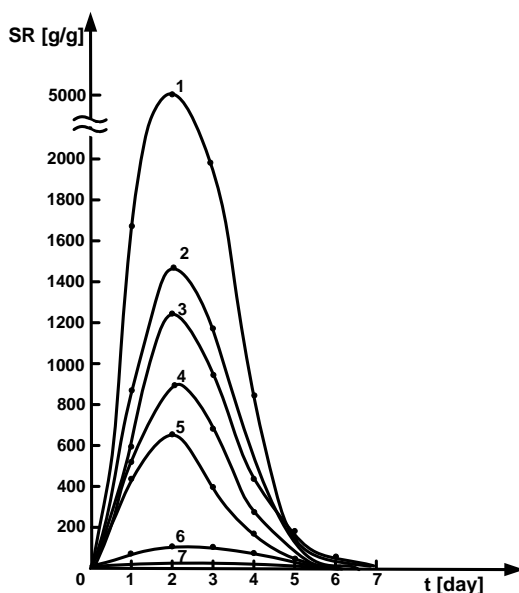


Fig. 6. Kinetics of water absorption and release capacity of PAHs (curve 1), BPAHs with 1,3,5,7,10 wt% of bentonite (curves 2-6 respectively), PAHs containing *N,N'*-methylenebisacrylamide (curve 7).

Fig. 6 shows the kinetic curves of water absorption capacity of PAHs, BPAHs with different wt% of bentonite colloidal solutions, and PAHs containing *N,N'*-methylenebisacrylamide. As presented above, the maximum water absorption of the PAHs accounts for 5000 g of water per 1 g of a dry hydrogel (curve 1). As seen in Fig. 6, the maximum absorption of the BPAHs is achieved at a bentonite concentration of 1%. With an increase in the concentration of ultrafine bentonite, absorptive capacity of the hydrogels decreases. It should be noted that the goal of synthesizing BPAHs was to lower the absorption and release of water and pharmaceuticals in PAHs which, in turn, are of particular interest for the manufacture of pharmaceuticals for prolonged action with a hydrogel carrier (data on the application of PAHs for making prolonged action pharmaceuticals will be presented in the upcoming article).

Introducing *N,N'*-methylenebisacrylamide with the ratios of AAm: *N,N'*-methylenebisacrylamide = 1.65:0.1 and 1.25:0.5 to the system allows one to obtain PAHs with water absorption 1.6 g/g and 0.6 g/g, respectively (Fig. 6, curve 7). An increase in the concentration of *N,N'*-methylenebisacrylamide leads to a decrease in the hydrogel absorbability. Changing the concentration of *N,N'*-methylenebisacrylamide makes it possible to regulate and adjust the density of polymer networks.

The samples of the PAHs and BPAHs, synthesized by FP, were analyzed by DSC (DSC Q-1500D); the results compiled and presented in Fig. 7.

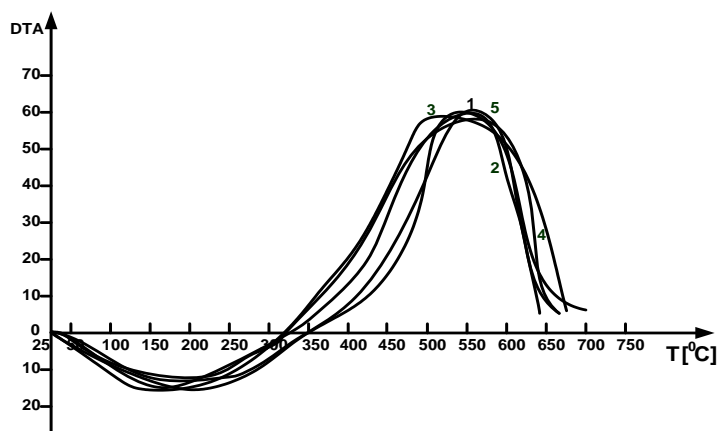


Fig. 7. Differential-thermal analysis of PAHs (curve 1), BPAHs with 3, 5, 7 wt% of bentonite (curves 2-4, respectively), and PAHs containing N,N'-methylenebisacrylamide (curve 5).

The results indicate that the samples of the PAHs are resistant up to 350°C (curve 1), and those of the BPAHs – up to 320°C (curves 2-4). Upon reaching these temperatures, the samples start to decompose.

PAHs containing 5% of bentonite were also synthesized varying the initial concentration ratios of AAm and Na acrylate (AAm:Na acrylate = 1:2.5; 1.75:1.75; 2.5:1). The results are demonstrated in Fig. 8.

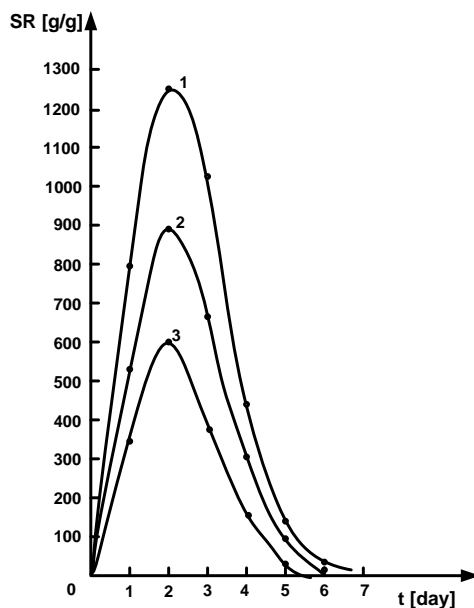
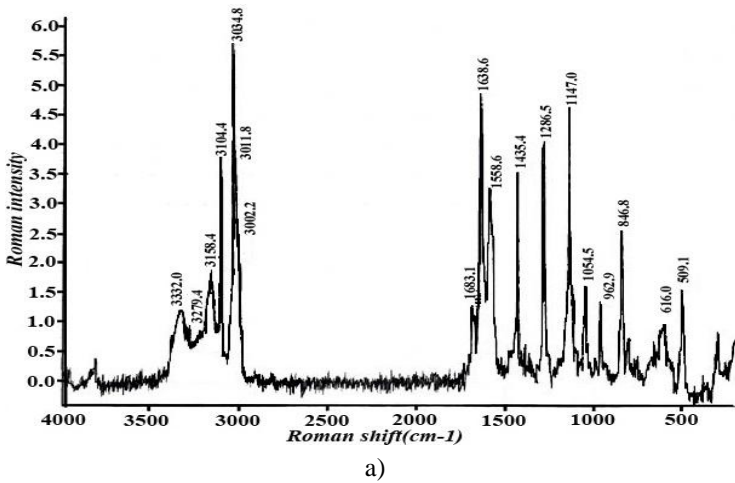


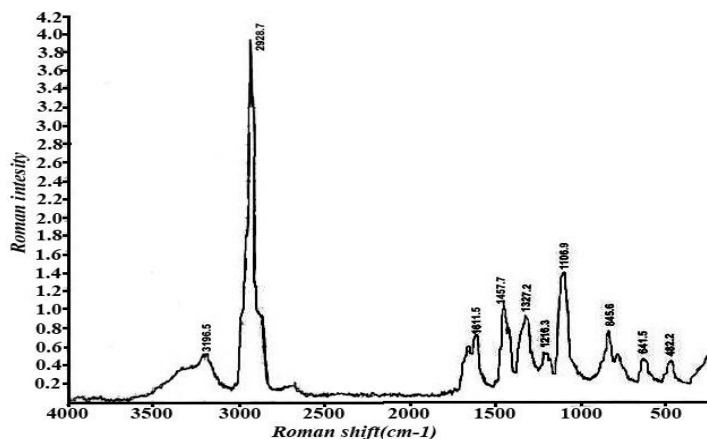
Fig. 8. Kinetics of water absorption and release capacity of PAHs containing 5 wt% of bentonite with different concentration ratios of the monomers: AAm:Na acrylate = 1:2.5 (curve 1), AAm:Na acrylate = 1.75:1.75 (curve 2), AAm:Na acrylate = 2.5:1 (curve 3).

As it can be seen from the curves, in the presence of 5% bentonite the PAHs' water absorbability depends on the ratio of the initial concentrations of the monomers. Here, the maximum water absorbability is observed at the ratio of AAm:Na acrylate = 1:1.25 (Fig. 8 , curve 1).

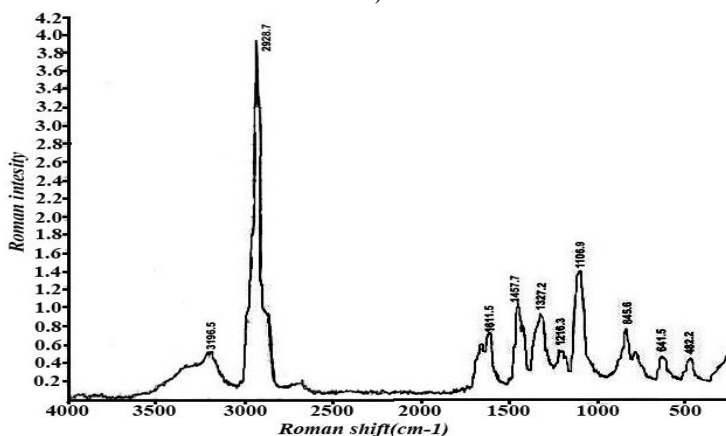
At the same time, a serious issue has recently arisen on the synthesis of PAHs, because of which many countries have ceased using PAHs in biology, medicine, agriculture and other spheres of human activities. In recent years it was found that the presence of even trace amounts of the primary monomer, toxic AAm, in PAHs can be harmful to health and the environment. The presence of residual AAm in PAHs is resulted from today's technologies and methods of PAH's production. It should be noted that the synthesis of PAHs by the method of FP completely eliminates the presence of AAm in the resulting hydrogels. This is due to the specificity of FP, i.e. the presence of a shock heat wave in the direction of the polymerization reaction, which, similar to the synthesis of superconducting high-temperature intercalated polymer nanocomposites, pushes residual amounts of the initial monomers into the polymerizing part of FP [32].

The absence of acrylamide in the obtained hydrogels was substantiated by the methods of Roman-spectroscopy (Fig. 9) and gel-chromatography (Fig. 10).





b)



c)

Fig. 9. Roman spectra of a) acrylamide, b) crystalline polyacrylamide, c) polyacrylamide hydrogel.

The comparison of the Roman spectra of acrylamide, crystalline polyacrylamide and polyacrylamide hydrogel, as well as the interpretation of the data obtained from the-gel chromatography shows that the synthesized PAHs are completely free of residual acrylamide.

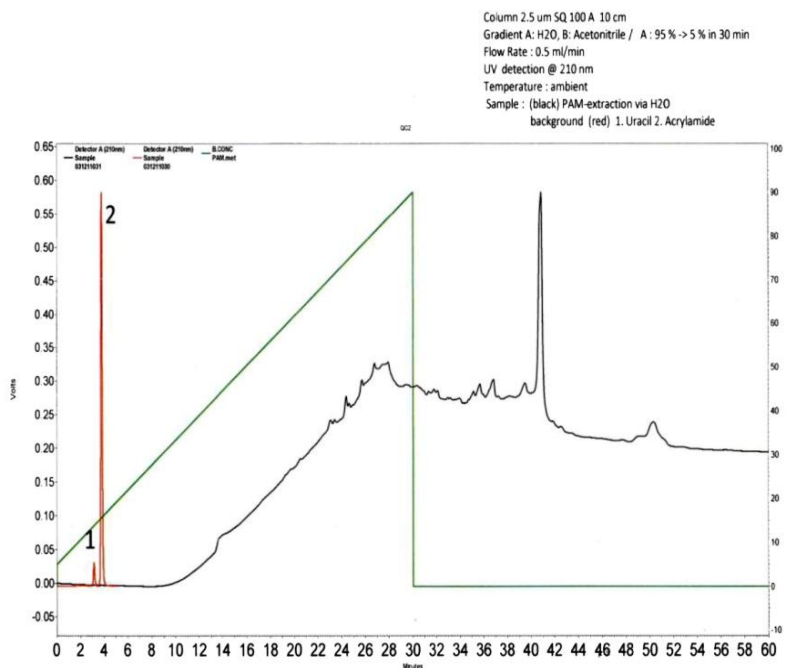


Fig. 10. Data obtained from gel-chromatography.

Conclusion

The paper demonstrates the advantages and achievements of FP in the synthesis of PAHs – high energy- and cost-efficiency, ecological purity, ability to provide high-quality PAHs, absolute non-toxicity (in contrast to the PAHs currently available in international practice) and possibilities of producing PAHs with prescribed properties through the regulation of the kinetic and macrokinetic parameters of the process. Thus, the synthesis of PAHs by FP is much cheaper than that by the traditional methods, and the characteristics of the product far exceed those available today. A particular advantage of the FP method is the possibility of synthesizing PAHs completely free of acrylamide.

Thus, as it can be derived from the presented material, the synthesis of hydrogels by the FP method provides a number of advantages in comparison with the conventional methods – the possibility of producing PAHs with prescribed properties, as well as PAHs completely free of residual toxic acrylamide.

Acknowledgments

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**ՃՐՈՆՏԱԼ ՊՈԼԻՄԵՐԱՑՄԱՆ ԵՂԱՆԱԿՈՎ ՆԱԽԱՊԵՍ ՏՐՎԱԾ
ՆԱԿԱՌԹՅՈՒՆՆԵՐՈՎ ՊՈԼԻԱԿՐԻԼԱՄԻԴԱՅԻՆ ՏԻԴՐՈԳԵԼԵՐԻ
ՄԻՆԹԵԶ**

**Ա. Ն. ՏՈՆՈՅԱՆ, Ա. Զ. ՎԱՐԴԵՐԵՍՅԱՆ, Դ. Ս. ԴԱՎԹՅԱՆ, Ա. Գ. ԷԵՏՅԱՆ,
Ա. Ն. ՄԻՆԱՍՅԱՆ և Ս. Պ. ԴԱՎԹՅԱՆ**

Վերջին մի քանի տասնամյակներում պոլիակրիլամիդային հիդրոգելերը (ՊԱԳ) հանդիսանում են ակտուալ և պահանջված ուսումնասիրման թեմաներից ամենատարբեր գիտական ասպարեզներում՝ քիմիա, ֆիզիկա, կենսաբանություն, բժշկություն և այլն: ՊԱԳերը կարված պոլիմերային կառույցներ են, որոնք ունակ են ուռչել՝ մեծ քանակի ջուր կլանելով և կլանած նյութերը արտանետել շրջակա միջավայր՝ առանց ձևի փոփոխության: Շնորհիվ այդ հատկությունների ՊԱԳերը պահանջված են գյուղատնտեսություն, կենսաինժեներիայում, կոսմետոլոգիայում, դեղագործություն, բժշկության, պլաստիկ վիրաբուժության, հիգիենայի պարագաների ստեղծման (տակդիրներ) բնագավառում և այլն:

Ներկայացված աշխատանքը նվիրված է ֆրոնտալ պոլիմերացման (ՖՊ) մեթոդով նախապես տրված հատկություններով ՊԱԳերի սինթեզի կինետիկայի և մակրոկինետիկայի ուսումնասիրությանը: Աշխատանքում ցույց է տրված, որ մեր կողմից առաջարկված մեթոդը ապահովում է պրոցեսի կառավարելիությունը և համապատասխանաբար ստացված ՊԱԳերի հատկությունները՝ համաձայն նախապես տրված պահանջներին՝ ջրի կլանման և արտանետման՝ 0,2 գ-ից մինչև 5000 գ հաշված 1գ չոր հիդրոգելի համար և պահանջվող ֆիզիկամեխանիկական հատկությունների՝ էլաստիկություն, մեխանիկական ամրություն, մեծ մեխանիկական բեռնվածության դիմանալու հատկություն, ընդ որում առանց փչրվելու:

Հատուկ նշենք, որ ի տարբերություն ներկայումս ավանդական եղանակով ստացվող ՊԱԳերի, մեր կողմից առաջարկվող մեթոդը ապահովում է ՊԱԳի բացարձակ էկոլոգիական անվտանգություն՝ ամբողջությամբ գերծ մնացորդային թունավոր մոնոմերի՝ ակրիլամիդի, նույնիսկ հետքերից:

**СИНТЕЗ ПОЛИАКРИЛАМИДНЫХ ГИДРОГЕЛЕЙ С ЗАРАНЕЕ
ЗАДАННЫМИ СВОЙСТВАМИ МЕТОДОМ ФРОНТАЛЬНОЙ
ПОЛИМЕРИЗАЦИИ**

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Полиакриламидные гидрогели (ПАГ) в последние несколько десятилетий являются одной из актуальнейших и востребованных тем исследований в самых разных научных дисциплинах: химии, физике, биологии, медицине и т.д. ПАГ — это сшитые полимерные структуры, способные набухать с поглощением большого количества влаги и отдавать обратно поглощенные вещества в окружающую среду без разрушения оригинальной формы. Благодаря этим свойствам ПАГ востребованы в сельском хозяйстве, биоинженерии, фармакологии, медицине, косметологии, пластической хирургии, в области создания предметов общей гигиены, вплоть до изготовления памперсов и др.

Представленная работа посвящена исследованию кинетики и макрокинетики синтеза ПАГ методом фронтальной полимеризации с возможностью получения продукта с заранее заданными свойствами. В работе показано, что предложенный нами метод обеспечивает управляемость процесса и, соответственно, свойств полученных ПАГ, согласно заранее заданным требованиям по набуханию и отдаче воды от 0.2 г до 5000 г воды на 1 г сухого гидрогеля и требуемым физико-механическим свойствам – эластичность, механическую упругость, способность выдерживать высокие механические нагрузки (при этом не рассыпаться).

Особо отметим, что, в отличие от получаемых в настоящее время традиционными методами ПАГ, предложенный нами метод обеспечивает абсолютную экологическую безопасность продукта, полностью свободного даже от следов остаточного ядовитого мономера – акриламида.

REFERENCES

- [1] Gels Handbook, Four-Volume Set, 1st Edition, eBook ISBN: 9780080532349, Elsevier, 2000.
- [2] Fuli Zhao, Dan Yao, Ruiwei Guo, Jianhua Zhang // *Nanomaterials*, December 2015(4):2054-2130, DOI: 10.3390/nano5042054.
- [3] Tang Q., Wu J., Lin J., Sun H., Ao H. // *e- Polymers*, 2008, №021.
- [4] Begishev V.P., Volpert V.A., Davtyan S.P., Malkin A.Ya. // *Dokl. Akad. Nauk SSSR*, 1973, v. 208, p. 892.
- [5] Tonoyan A.O., Prikhonenko A.I., Davtyan S.P., Milman V.D., Rozenberg B.A., Enikolopyan N.S. // *Dokl. Akad. Nauk SSSR*, 1973, v. 211, №4, p.673.
- [6] Tonoyan A.O., Harutyunyan Kh. A., Davtyan S.P., Rozenberg B.A., Enikolopyan N.S. // *Visokomolek. Soed.*, 1974, XVI B, №11, p.799.
- [7] Tonoyan A.O., Leykin A.D., Davtyan S.P., Rozenberg B.A., Enikolopyan N.S. // *Visokomolek. Soed.*, 1974, A16, p. 1847.
- [8] Kuvarina N.M., Tonoyan A.O., Davtyan S.P., Aleksanyan G.G., Prut E.V., Jarov A.A., Enikolopyan N.S. // *Visokomolek. Soed.*, 1974, A16, p. 1005.
- [9] Aleksanyan G.G., Harutyunyan Kh.A., Bodneva V.L., Prut E.V., Davtyan S.P., Rozenberg B.A., Shkadinski K.G., Enikolopyan N.S. // *Visokomolek. Soed.*, 1975, A17, p. 913.
- [10] Surkov N.F., Davtyan S.P., Rozenberg B.A., Enikolopyan N.S. // *Dokl. Akad. Nauk SSSR*, 1977, v. 232, p. 64.
- [11] Turusov R.A., Shkadinski K.G., Davtyan S.P., Rozenberg B.A., Andreevskaya G.D., Enikolopyan N.S. // *Dokl. Akad. Nauk SSSR*, 1979, v. 247, p. 97.
- [12] Davtyan S.P., Gelman E.A., Gelman A.A., Karyan A.A., Tonoyan A.O., Enikolopyan N.S. // *Dokl. Akad. Nauk SSSR*, 1980, v. 253, p. 380.
- [13] Volpert V.A., Davtyan S.P. // *Phizika gorennya i vzryva*, 1985, №2, p. 8.
- [14] Davtyan S.P., Jijin G.V., Segal A.G. // *Kinetika i kataliz*, 1986, v. 26, №6, p. 1310.
- [15] Babajanyan A.S., Volpert V.A., Volpert V.I., Megrabova I.N., Davtyan S.P. // *Phizika gorennya i vzryva*, 1988, №1, p. 27.
- [16] Babadzhanian A.S., Volpert V.A., Volpert V.I., Megrabova I.N., Davtyan S.P. // *Combustion, Explosion, and Shock Waves*. 1989; 25(1):23-31.
- [17] Bostandzhyan S.A., Shulikovskaya M.V., Davtyan S.P. // *Theoretical Foundations of Chemical Engineering* v. 23, Issue 3, January 1990, p. 223.
- [18] Solov'yev S.E., Volpert V.A., Surkov N.F., Davtyan S.P. *Khimicheskaya fizika*, 1991, v.10, №10, p. 1348.
- [19] Volpert V.A., Volpert V.I., Davtyan S.P., Megrabova I.N., Surkov N.F. // *SIAM Journal on Applied Mathematics*, 1992, v. 52(2), p. 368.
- [20] Solov'yev S.E., Volpert V.A., Davtyan S.P. // *SIAM. J.Appl.Math.* 1993, v. 53, p. 907.
- [21] Volpert V.A., Volpert V.I., Pojman J. A. // *Chem. Eng. Sci.*, 1994, v. 14, p. 2385.

- [22] *Guo Dong Lu, Qing Zhi Yan, Chang Chun Ge* // Polymer International SCI, V.56, Issue 8, August 2007, p. 1016.
- [23] *Scognamillo S., Alzari V., Nuvoli D., Mariani A.* // Published online in Wiley Interscience 10 March 2010, DOI: 10.1002/pola.24020.
- [24] RA Patent № 2235A, S. Davtyan, A. Tonoyan, L. Gevorgyan, 2008.
- [25] *Tonoyan A.O., Gevorgyan L.A., Alaverdyan G.Sh., Kurtikyan T.S., Davtyan S.P.* // Semiconductor micro- and nanoelectronics, Proceedings of the 7th International Conference, Tsakhcadzor, Armenia, July 3-5, 2009, p. 90.
- [26] *Chilingaryan A.S., Gevorgyan L.A., Voskanyan H.S., Tonoyan A.O.* // i-PolyMat 2010, May 16-19, Kerkrade, NL.
- [27] RA, Patent N 2697A, S. Davtyan, A. Tonoyan, L. Gevorgyan, A. Varderesyan, 2012.
- [28] *Tonoyan A.O., Petrosyan V.A., Davtyan S.P., Aleksandryan A.V.* // European Science and Technology, Materials of the XIII International Research and Practice Conference, Munich, Germany, 2016, p. 39.
- [29] *Aleksandryan Anahit, Tonoyan Anahit, Davtyan Sevan* // SETAC Europe 26th Annual Meeting, 2016, CONTROL ID 33751.
- [30] *Varderesyan A.Z.* // High-Performance Polymers for Engineering-Based Composites. Corporate Book, 2016, p. 39.
- [31] *Davtyan S.P., Tonoyan A.O.* Teoriya i praktika adiabaticheskoy i frontalnoy polimerizacii (Theory and practice of adiabatic and frontal polymerization). Monograph. Palmarium Academic Publishing, 2014, 660 p.
- [32] *Tonoyan A.O., Davtyan S.P.* // High-temperature superconducting ceramic nanocomposites in Ceramic Nanocomposites Book, Woodhead Publishing Limited 2013, p. 284.