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СИНТЕЗ ГИДРОГЕЛЕЙ ПОЛИАКРИЛАМИДА С ПОРФИРИНОВЫМИ ФРАГМЕНТАМИ В БОКОВОЙ ЦЕПИ В ПРИСУТСТВИИ ИМИДАЗОЛИЕВЫХ ИОННЫХ ЖИДКОСТЕЙ

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Методом радикальной полимеризации в растворе синтезированы акриламидные гидрогели, содержащие в своем составе порфириновые фрагменты. Синтез проводили в присутствии имидазолиевых ионных жидкостей с длиной алкильного заместителя в имидазолиевом кольце от С4 до С8. Установлено влияние используемых ионных жидкостей на структуру и некоторые свойства полученных порфиринсодержащих акриламидных гидрогелей. Введение в реакционную систему ионной жидкости с различной длиной алкильного заместителя способно оказывать влияние на структурные изменения, происходящие с порфириновым сомономером в процессе сополимеризации с акриламидом. В реакционной среде в присутствии ионной жидкости наблюдается ингибирование образования бактериохлориноподобных структур. Наиболее заметно этот эффект проявляется с использованием имидазолиевой ионной жидкости с длиной алкильного заместителя С8. Установлено, что гидрогели, полученные в присутствии имидазолиевых ионных жидкостей, обладают меньшей удельной поверхностью по сравнению с гидрогелями, полученными без использования ионных жидкостей. Наименьшие значения удельной площади поверхности показали гидрогели, синтезированные с использованием 1-октил-3-метилимидазолия бромида. Также обнаружено, что введение ионной жидкости при проведении сополимеризации акриламида с порфириновым мономером в растворе может способствовать как увеличению, так и уменьшению численных значений сорбционных характеристик получаемых гидрогелей в зависимости от длины алкильного заместителя в имидазолиевом кольце и соотношения порфирин : акриламид. Наибольшей степенью набухания обладают гидрогели, синтезированные с использованием 1-гексил-3-метилимидазолия бромида и 1-октил-3-метилимидазолия бромида при исходном соотношении порфирин : акриламид равным 1:20. Варьирование соотношения исходных мономеров, структуры имидазолиевой ионной жидкости в процессе сополимеризации позволяет контролировать физико-химические характеристики получаемых порфиринсодержащих гидрогелей, которые могут быть полезны для решения различных прикладных задач.

Ключевые слова: гидрогели полиакриламида, порфиринполимеры, порфириновые мономеры, ионные жидкости, сорбционные свойства

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SYNTHESIS OF POLYACRYLAMIDE HYDROGELS WITH PORPHYRIN FRAGMENTS IN THE SIDE CHAIN IN THE PRESENCE OF IMIDAZOLIUM IONIC LIQUIDS

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The acrylamide hydrogels containing the porphyrin fragments have been obtained by radical polymerization in a solution. The synthesis has been carried out in the presence of imidazolium ionic liquids with length of the alkyl substituent in the imidazolium ring from C4 to C8. The influence of the used ionic liquids on the structure and some properties of the resulting porphyrin-containing acrylamide hydrogels has been established. The addition of an ionic liquid with a different length of the alkyl substituent into the reaction system can influence the structural changes that occur with the porphyrin comonomer during copolymerization with acrylamide. The formation of bacteriochlorin-like structures is inhibited in the presence of an ionic liquid in the reaction medium. This effect is most noticeable when using an imidazolium ionic liquid with a C8 alkyl substituent length. Hydrogels synthesized in the presence of ionic liquids have lower specific surface area compared to ones obtained without the use of ionic liquids. The lowest specific surface area values were shown by hydrogels synthesized using 1-octyl-3-methylimidazolium bromide. It was also found that the introduction of ionic liquid into the reaction mixture can contribute to both increase and decrease in the numerical values of the sorption characteristics of the resulting hydrogels, depending on the length of the alkyl substituent in the imidazolium ring and a porphyrin : acrylamide ratio. Hydrogels synthesized using 1-hexyl-3-methylimidazolium bromide and 1-octyl-3-methylimidazolium bromide at an initial porphyrin : acrylamide ratio of 1:20 have the highest degree of swelling. Varying the ratio of the initial monomers and the structure of the imidazolium ionic liquid during the copolymerization process allows to control the physicochemical characteristics of the resulting porphyrin-containing hydrogels, which can be useful for solving various applied problems.

Keywords: polyacrylamide hydrogels, porphyrin polymers, porphyrin monomers, ionic liquids, sorption properties

INTRODUCTION

The hydrogels are a class of the polymeric materials with a three-dimensional structure, which are able to hold large amount of water. [1-3]. In recent decades, the hydrogels have attracted scientific and industrial interest due to their high water absorption, biocompatibility, and biodegradability [4-6]. These unique materials have found application for biomedical purposes, including drug delivery systems [7-14], wound dressings [15, 16], tissue engineering materials [17-20], smart materials and various sensors [21-28], cosmetic and agricultural products [29, 30].

The hydrogels can include not only hydrophilic, but also hydrophobic units, which are capable of swelling and interacting with both aqueous and organic solutions. These hydrogels are able to encapsulate hydrophobic molecules under certain conditions, which determines their use in pharmacology [9]. The use of the tetrapyrrole macroheterocyclic compounds, for example, porphyrins and phthalocyanines, which have biological, catalytic, photo-, and antimicrobial activity [31] for modifying hydrogels, is of interest in order to create promising materials for various applications. In this case, the swelling behavior and properties of the hydrogels will be influenced by the reaction medium, the nature of the polymer and porphyrin.

Recently, the ionic liquids (ILs) of various natures have been actively used as a replacement for traditional solvents in organic synthesis [32, 33], in particular, for the synthesis of the polymers [34, 35]. Varying the synthesis parameters will affect the properties

and a structure of the resulting hydrogels, which will make it possible to synthesize the hydrogel materials with predetermined characteristics to solve specific problems.

Consequently, in this short communication the influence of imidazolium ionic liquids on the structure and some physicochemical properties of the hybrid hydrogels based on acrylamide and mono-*meso*-allyloxy-substituted porphyrin was investigated.

EXPERIMENTAL

Materials and methods

Acrylamide (AA) (Sigma-Aldrich, 98%) was used to prepare the hydrogels. Azobiisobutyric acid dinitrile (AIBN) (Vecton, purity > 98%) was used as a radical polymerization initiator. The reagents were purified according to the procedure [36]. The crosslinking agent N,N'-methylene-*bis*-acrylamide (MBA) (abcr GmbH, purity > 97%) was recrystallized from acetone. Methylimidazole and corresponding bromoalkanes were used to synthesize 1-butyl-3-methylimidazolium bromide C_1C_4ImBr (**I**), 1-hexyl-3-methylimidazolium bromide C_1C_6ImBr (**II**), 1-octyl-3-methylimidazolium bromide C_1C_8ImBr (**III**) [37, 38]. 5-(4'-Allyloxy)-phenyl)-10,15,20-triphenylporphyrin (P), used as a porphyrin comonomer, was by the method in [39]. 1,4-Dioxane (Vecton, analytical grade) was kept over KOH for 24 h, then purified by distillation at atmospheric pressure.

The synthesis of the porphyrin-containing hydrogels was carried out by radical copolymerization in a solution using a water bath shaker SWT-100. Electronic reflection spectra of the porphyrin-containing hydrogels were recorded on a SHIMADZU UV-2550 spectrophotometer with a diffuse reflection attachment.

The specific surface area of the hydrogels was studied by a Sorbi®-MS installation, designed for measuring the specific surface area of dispersed and porous materials.

Thermogravimetric analysis (TGA) of the hydrogels was performed by a Jupiter instrument STA 449 F3. Samples weighing 3-5 mg have been heated from 30 to 600 °C at a heating rate of 10 °C/min under a continuous stream of argon.

Synthesis of hydrogels

AIBN (0.006 mmol) and MBA (0.16 mmol) were added to a 10 ml test tube to a solution of acrylamide (1.41 mmol) and the porphyrin monomer in the mass ratio P:AA = 1:20, 1:10 or 3:20 in a mixture of IL:dioxane = 1:40. The reaction mixture was kept in a nitrogen atmosphere for 20 min, then the test tube was placed in a shaker bath. The synthesis was carried out at 70 °C and constant stirring (70-80 rpm) for 4 h. The resulting precipitate was filtered off, washed with chloroform until the filtrate was clear, and dried at 50 °C.

Determination of the gel fraction and sorption characteristics of hydrogels

The gel fraction of samples was determined according to the following formula [40 – 43]:

$$GF = \frac{m_{dry}}{m_0} \cdot 100\% \qquad (1),$$

where m_0 is the weight of the dry sample before extraction, m_{dry} is the weight of the dried gel fraction after extraction.

The degree of swelling (SR, %) and the water content (WC, %) of the hydrogels were determined by the following formulas [41, 44-46]:

$$SR = \frac{m_s - m_{dry}}{m_{dry}} \cdot 100\% \qquad (2),$$

$$WC = \frac{m_w}{m_s} \cdot 100\% \qquad (3),$$

$$m_w = m_s - m_{dry},$$

where m_w is the weight of water in the gel, m_s is the weight of the swollen gel, m_{dry} and m_s are the masses of dry and swollen hydrogel, respectively.

RESULTS AND DISCUSSION

The synthesis of the porphyrin-containing hydrogels has been carried out in dioxane with the addition of the dialkylimidazolium ionic liquids (**I-III**), differing in the length of the alkyl substituent in the imidazolium ring. It was found that non-crosslinked water-soluble structures are predominantly formed with an increase in the ionic liquid content in a IL:dioxane ratio. The optimal IL:dioxane ratio, at which acrylamide hydrogels with the maximum gel fraction are formed, has been selected experimentally as 1:40, respectively. The copolymers synthesized in a dioxane environment without the use of IL were applied as reference samples.

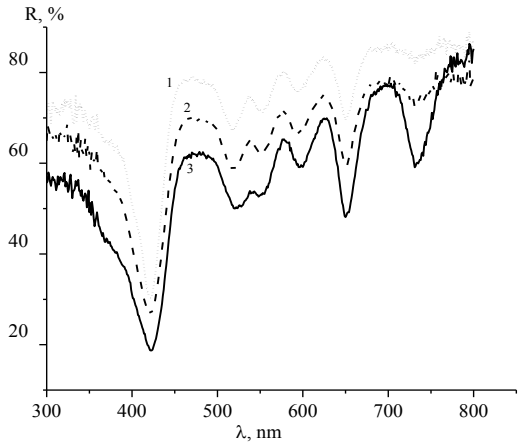

Fig. 1. Electronic reflectance spectra of the hydrogels (P:AA = = 1:10) synthesized using imidazolium ILs: 1 – C_1C_8ImBr (**III**); 2 – C_1C_6ImBr (**II**); 3 – C_1C_4ImBr (**I**)

Рис. 1. ЭСО гидрогелей (соотношение P:AA = 1:10), полученных с использованием имидазолиевых ИЖ: 1 – C_1C_8ImBr (**III**); 2 – C_1C_6ImBr (**II**); 3 – C_1C_4ImBr (**I**)

As was shown earlier [47, 48], the porphyrin monomers included in the polymer chain undergo structural changes: the formation of chlorine- and bacteriochlorine-like structures occurs during the synthesis of the acrylamide hydrogels. These changes are expressed by the appearance of an absorption band in the region of 730 nm and an increase in the intensity of the absorption band at 650 nm in the electronic reflection spectra of the hydrogels, as well as in the electronic absorption spectra of the water-soluble low-molecular fractions. Similar effects have been found for compounds obtained in an IL-solvent medium. Thus, an increase in the intensity of the band in the region of 650 nm and the appearance of an absorption band at 730 nm are observed in the electronic reflectance spectra of the synthesized hydrogels. However, the formation of bacteriochlorine-like structures is inhibited under the conditions of hydrogels synthesis using the imidazolium ILs (**II**) and (**III**). This is detected by a decrease in the intensity of the absorption band in the region of 730 nm (Fig. 1). The use of IL (**I**) does not inhibit the formation of such structures during the synthesis of the hydrogels in contrast to ILs (**II**) and (**III**). Thus, the introduction of the ILs with different lengths of the alkyl substituent can influence the structural changes that occur with the porphyrin comonomer during the copolymerization with acrylamide.

The specific surface area of the resulting hydrogels was also studied. The obtained data on the specific surface area of hydrogels synthesized in dioxane and in an IL:dioxane mixture are presented in Table 1.

Table 1

Specific surface area of the synthesized hydrogels
***Таблица 1*. Удельная площадь поверхности синтезированных гидрогелей**

IL	Specific surface, m^2/g		
	P:AA 1:20	P:AA 1:10	P:AA 3:20
—	87,5	85,4	80,6
I	49,8	41,6	53,8
II	54,8	53,6	54,2
III	17,0	12,8	20,5

The hydrogels synthesized in a dioxane medium have a more developed specific surface area compared to the compounds synthesized in an IL:dioxane mixture. The use of C_1C_6ImBr (**II**) for the synthesis of the hydrogels makes it possible to obtain the compounds with almost identical specific surface area values, ranging from 53-55 m^2/g, regardless of the amount of the initial porphyrin in the P:AA ratio. The hydrogels synthesized using C_1C_8ImBr (**III**) have the lowest specific surface area.

The gel fraction of the hydrogels was calculated according to formula (1). The gel fraction ranged from 55% to 84% depending on a ratio of P:AA and IL:dioxane. The results obtained are presented in Table 2.

Table 2

The gel fraction of the synthesized hydrogels
***Таблица 2*. Гель-фракция синтезированных гидрогелей**

IL	GF, %		
	P:AA 1:20	P:AA 1:10	P:AA 3:20
—	88	86	85
I	84	60	55
II	72	69	84
III	74	74	77

Table 3

Sorption properties of the synthesized hydrogels
***Таблица 3*. Сорбционные характеристики синтезированных гидрогелей**

IL	SR, %			WC, %		
	P:AA 1:20	P:AA 1:10	P:AA 3:20	P:AA 1:20	P:AA 1:10	P:AA 3:20
—	1248	1108	1040	93	92	91
I	1196	1150	1261	92	92	93
II	1294	1110	977	93	92	91
III	1343	933	1122	92	90	92

The gel fraction of the hydrogels synthesized without adding ILs is in the range of 85-88%. The effect of ILs on the gel fraction of the synthesized hydrogels is ambiguous. The addition of the IL (**I**) into the reaction system leads to a decrease in the gel fraction of the hydrogels with an increase in the amount of porphyrin in the P:AA ratio. The gel fraction of hydrogels to increase from 60 to 74% with a rise in the length of the alkyl substituent in the IL and at the mass ratio P:AA = 1:10. The gel fraction of the hydrogels obtained in the presence of C_1C_6ImBr (**II**) and C_1C_8ImBr (**III**) reaches maximum values at the mass ratio P:AA = = 3:20 and is equal to 84% and 77%, respectively.

Such sorption characteristics as the hydrogels swelling degree (SR, %) and the water content (WC, %) were calculated using formulas (2) and (3), respectively. The data are presented in Table 3.

The WC of the hydrogels obtained both in the presence of the ILs (**I-III**) and without them are almost the same. The swelling degree of the hydrogels synthesized in dioxane is significantly influenced by the amount of the porphyrin in the P:AA ratio. An Increase in the porphyrin content in the P:AA ratio leads to a decrease in the swelling degree of the hydrogels. The use of the ILs (**I-III**) for the synthesis of the hydrogels effects the SR index differently. The swelling degree

of the hydrogels grows from 1196 to 1343% with an increase in the length of the alkyl substituent in the IL and at the ratio P:AA = 1:20. The hydrogels swelling degree decreases at other P:AA ratios. An Increase in the content of the porphyrins in the P:AA ratio leads to a decrease in SR values when using ILs (**I-III**). The water content in the hydrogels varies from 90-93%.

To determine the thermal stability of the resulting compounds, the thermogravimetric analysis was carried out.

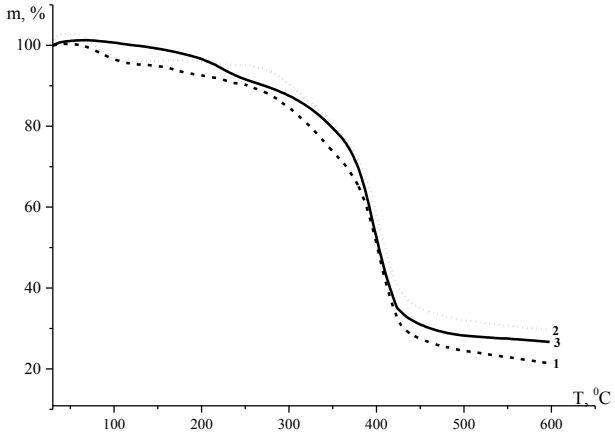

Fig. 2. The thermogravimetric curves: 1 – the cross-linked unmodified polyacrylamide hydrogel; 2 – the hydrogel synthesized in a dioxane medium at a ratio of P:AA = 1:20; 3 – the hydrogel synthesized in C1C8ImBr:dioxane medium at a ratio of P:AA = 1:20

Рис. 2. Термогравиметрические кривые: 1 – сшитый немодифицированный полиакриламидный гидрогель; 2 – гидрогель, полученный в среде диоксана при соотношении P:AA = 1:20; 3 – гидрогель, полученный в среде C1C8ImBr:диоксан при соотношении P:AA = 1:20

Fig. 2 shows the thermogravimetric curves of the unmodified cross-linked polyacrylamide, the porphyrin-containing hydrogels obtained in a dioxane environment and in a C_1C_8ImBr:dioxane environment at a ratio of initial components P:AA = 1:20. The initial weight reduction for all samples occurs when heated to 100-105 °C by approximately 5%, which is due to the release of a bound water from the hydrogel. The nature of the thermogravimetric curves practically does not change with further heating of the hydrogels. The porphyrin-containing hydrogels are quite stable when the temperature increases from 100 to 250 °C. Next, there is a gradual decrease in the weight of the hydrogels after 250 °C up to 360 °C with a weight loss of about 20%. Then a sharp decrease in weight is observed with a loss of up to 70%, followed by decomposition of the samples after 420 °C. Porphyrin-containing hydrogels show less weight loss compared to unmodified hydrogel.

Thus, thermogravimetric analysis confirmed that the resulting hydrogels are quite stable, the decomposition of samples begins at 250 °C and reaches a maximum at 400-420 °C.

CONCLUSIONS

Thus, it was found that the addition of the ionic liquids with different lengths of the alkyl substituent in the imidazolium ring to the initial reaction mixture can control side processes affecting the structure of the tetrapyrrole macroheterocyclic compounds during the synthesis of the modified polyacrylamide hydrogels, as well as influence some physicochemical properties of the resulting compounds. It was revealed that the nature of the IL used affects the gel fraction, as well as the sorption properties of the synthesized hydrogels. The gel fraction and the hydrogels swelling degree can either increase or decrease depending on the length of the alkyl substituent in the IL and the ratio of the initial reagents.

It is worth noting that the resulting hybrid compounds may be useful for various applications, for example, as potential antibacterial materials and catalysts.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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