Obtain of Carboxylic- and Aminocontaining Hydrogels Based on Acryl Amide

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Abstract – *Cross-linked hydrogels based on functional copolymers of acryl amide with either acrylic acid or dimethylaminoethyl methacrylate were synthesized. It was studied the influence of the comonomer ratio onto copolymerization kinetics as well as the dependence of the physicochemical and physicomechanical properties of hydrogels on copolymer nature and cross-linking degree. The hydrogel obtained are highly flexible and elastic materials. In terms of swelling rate and degree, they can be attributed to super absorbent polymers.*

Key words – *cross-linked hydrogels, functional copolymers, radical copolymerization, super absorbent polymers, swelling degree.*

I. Introduction

Industrial development requires the creation of new polymeric materials with predetermined properties. Required properties most easily achieved by the creation of expanded polymeric (composite) materials. A significant advantage of polymer composite materials to traditionally used materials are: the use of cheap raw materials, which has a strong base, saving a polymeric binder, improvement of technological and consumer properties.

But opportunities of composite contradictions are limited between the mechanical properties and surface energy of the filler and polymer matrix. The first one leads to stresses in the interfacial layers, and the second - to aggregate particulates. Both of these phenomena lead to a significant reduction of operating properties. Therefore, at the present stage to produce composite materials using only modified fillers. That is the relevance of this problem is to expand the range of fillers by a search for new and modification of known.

At the same time, the food industry and catering after frying different products are heavy overdone vegetable oil which is not suitable for use in food purposes. In this connection it is interesting to explore the possibility of using waste vegetable oil for surface modification of dispersed mineral fillers (chalk) for further use for filling polymer composites. Besides this chalk could be interesting to test in a filler with low water absorption for use in building materials.

II. Experimental

Synthesis crosslinked hydrogels carried out by radical copolymerization of acrylamide (AkAm) acrylic acid (AA) or dymetylaminoetyl¬metakrylatom (DMAEM) in an amount of 5-20 %mol. The process performed in aqueous solutions in sealed ampoules measured at a temperature of 333K. The concentration of monomers - 1.5 mol/l, which corresponded to the bottom line hydrogel - 11-12%. When copolymerization AkAm and AA used as the initiator ammonium persulfate which was dissolved in the aqueous phase. When copolymerization AkAm and DMAEM used as the initiator of the DAC, which was dissolved in the organic phase. The concentration of the initiator in both cases was $5 \cdot 10^{-3}$ mol/L. For crosslinked hydrogels used crosslinking agent is N, N'-methylene-bis-acrylamide (MBA), which was added to the reaction mixture in an amount of 0.5-2% of the monomers.

Conversion of monomers dilatometer determined by gravimetric and controlled. To determine the gel fraction crosslinked hydrogels they precipitated in methanol and dried to constant weight. Soluble fraction ekstrahuvalas Soxhlet apparatus in water for 12 hours. Gel fraction (g) determined by the formula:

$$g = (m_{ex}/m_0) \cdot 100\%, \qquad (1)$$

where m_{ex} - mass copolymer after extraction, m_0 - mass of the sample copolymer.

The kinetics of swelling of crosslinked hydrophilic copolymer was determined as follows. A sample of dry copolymer filled with water and kept for some time. Then neabsorbovanu poured water swollen hydrogel and unloaded on filter paper to remove neabsorbovanoyi water and then weighed. The degree of swelling was determined by the formula:

$$D. S. = ((m_{sw} - m_0)/m_0) \cdot 100\%, \qquad (2)$$

where mnabr - swollen copolymer weight, m0 - mass of the sample copolymer.

Elastic properties (the ability to compress) structured hydrogels was determined as follows: samples derived hydrogels in a cylinder diameter ~9 mm and a height of 10-12 mm were placed under the press. Measured the height of the sample at different loads. Strain determined by the formula:

$$\varepsilon = ((h_0 - h_{com})/h_0) \cdot 100\%, \qquad (3)$$

where h_0 - height hydrogel sample without load, h_{com} - the height of the loaded sample.

III. Results

The study of the kinetics of synthesis of crosslinked hydrophilic copolymer suggest that copolymerization comes with enough speed and with high conversion (97-99%), and the introduction of the crosslinking agent reaction was slightly affects the speed copolymerization.

The rate of copolymerization of acrylamide DMAEM much lower (almost an order of magnitude) than for AK - vapor AkAm/AA it is $(1,35-1,80 \cdot 10^{-02}$ mol/l•s), and for a couple AkAm/DMAEM $(1,20-1,95 \cdot 10^{-03}$ mol/l•s) with the same concentration of functional komonomeru (10% mol) and various concentrations of IBA. Moreover, the rate of copolymerization decreases with increasing content DMAEM in the reaction mixture.

Were obtained crosslinked hydrophilic polymers capable of swelling in water. The degree of crosslinking (gel fraction) increases with the crosslinking agent content of 59-65% at $C_{MBA}=0.5\%$ to 76-79% at $C_{MBA}=2.0\%$ and little depends on the nature of the functional komonomer.

Hydrogels based on both types of copolymers are characterized by an extremely high degree of swelling,

which, however, greatly depends on the nature of the functional komonomeru (Fig.1). So, if karboksylvmisnyh copolymers of poly (AkAm/AA) maximum degree of swelling for 24 hours. % of 2000-2500, for Amine Contain copolymers of poly (AkAm/DMAE), it is several times higher - 15000-17000%. Swelling rate is also higher for copolymers of hydrogels based on poly (AkAm/DMAE), for which the maximum degree of swelling is reached after 0.5 hrs., Then curve the degree of swelling of the time out on the plateau. In the case of hydrogels based on copolymers of poly (AkAm/AA) even after 2-5 hours. there has been some increase in the degree of swelling.

As expected, the degree of swelling decreases with increasing content in the system crosslinking agent. For copolymers based AK MBA with increasing content of 0.5 to 2%, the degree of swelling at T = 298K reduced from 2500% to 1400%, and Amine Contain copolymers - from 16000% to 8000%. This is obviously due to the formation of a more dense and rigid polymer mesh, which reduces the ability to cross-linked polymer swelling.
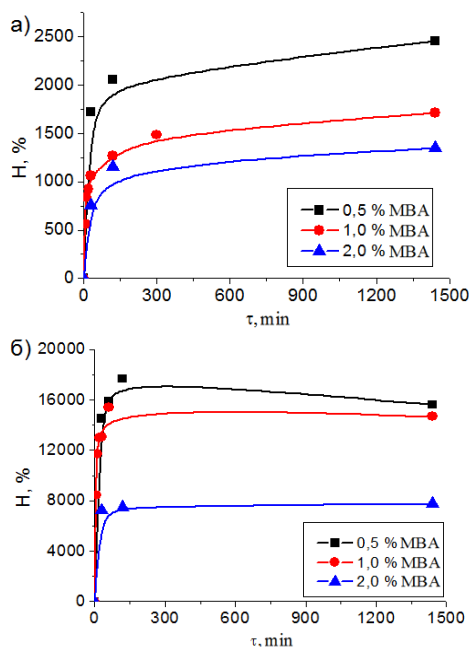

Fig. 1. Kinetic curves swollen copolymer poly (AkAm/ AA) (a) and poly (AkAm/DMAEM) (b) at a temperature T = 298K

Given that the swelling kinetics obeys the equation of the second order, the rate of swelling can be expressed by the equation:

$$\frac{dW}{dT} = K(W_\infty - W)^2 \qquad (4)$$

where W - water content hydrogels, W_∞ - equilibrium (maximum attainable) water content of the hydrogels, t - time K - rate constant swelling.

After integrating equation 4 obtained equation:

$$W = \frac{KW_\infty^2 t}{1 + KW_\infty t} \cdot \qquad (5)$$

What can be written as:

$$\frac{t}{W} = \frac{1}{KW_\infty^2} + \frac{t}{W_\infty} \qquad (6)$$

According to this equation the experimental data can be presented in a straight line slope is equal to $1/W_\infty$, and which cuts on the vertical axis section of $1/(K \cdot W_\infty^2)$. That is, depending on the graphic t/W~t, we can determine the rate constant and the equilibrium swelling (maximum attainable) water content of the hydrogels in the circumstances.

It is evident that the values are in good agreement with the results obtained from the swelling kinetic curves (Fig. 1). Swelling rate constant for copolymers Amine Contain 2 orders of magnitude greater than karboksylvmisnyh for both types of copolymers decreases with increasing content structuring agent. The maximum achievable water content hydrogels are also greater for Amine Contain copolymers and falls with increasing concentrations of MBA in the reaction mixture, which indicates a more structured, rigid hydrogel polymer frame.

The data show that the speed and the degree of swelling obtained hydrogels can be attributed to the polymers superabsorbuyuchyh, the degree and rate of swelling determined by the nature copolymer frame and crosslinking density (Fig. 1).

The resulting hydrogels are highly structured, elastic materials, which are also characterized by relatively high strength. Thus, when the compressive load to 16.5 kPa relative strain samples hydrogels are 25-48% depending on the degree of crosslinking and the copolymer composition without destroying the sample (Fig. 2). However, after removing the load samples completely restored shape and size, indicating the formation of strong mesh structure that does not collapse under load. The value of the maximum relative compression decreases with increasing concentration MBA, as in this case formed thicker mesh, which leads to increase stiffness swollen hydrogel.
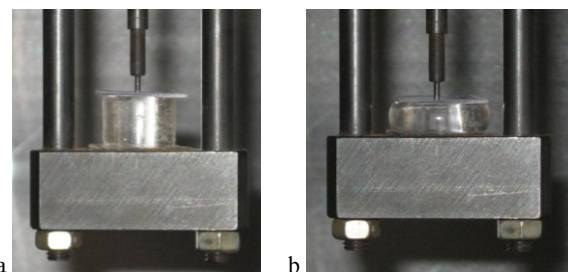

Fig. 2. Samples hydrogel n (AkAm-AA) (90:10) (C$_{MBA}$=0.5%) to load (a); load P = 16,5 kN / m^2 (b).

Conclusion

The radical copolymerization of hydrophilic functional monomers in an aqueous medium was obtained spatially crosslinked polymeric hydrogels. Research copolymerization kinetics indicate that the rate of vapor AkAm/AA approximately an order of magnitude higher than for couples AkAm/DMAEM. The speed and degree of swelling obtained hydrogels can be attributed to the polymers and superabsorbuyuchyh these parameters depend on the nature and extent copolymer frame stitching. The resulting hydrogels are highly structured, elastic materials that are highly durable and can restore the shape and size after removal of the load.

Synthesis of New Phosphoric and Amino Acid Derivatives Based on 4,6,4`,6` Hidrazo-Tetrachloro-Bis-1,3,5-Triazine

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Abstract – Interaction optimization techniques and synthesized new heterocyclic derivatives based on hidrazo bis-1,3,5-triazine of aminophosphorus and amino acid fragments. The optimum conditions of flow reactions. Determined and confirmed the structure obtained new heterocyclic triazine systems.

Key words – triazine, hydrazotriazine, amino acids, nucleophilic substitution.

I. Introduction

Triazine interest dates back to the XIX century when was first synthesized tsianur acid. According compound interest increases every year, it refers to as sim-triazine and bis-triazine. Mainly due to their use in various fields, including organic and pharmaceutical chemistry. As for the reactivity of cyanuric chloride and this derivatives in general, for them as for triazine inherent mainly nucleophilic substitution reactions. However, unlike triazine, transformation occurring with the opening cycle, they are not typical, and reactions do not know.

Also known triazine derivatives are used as intermediates for the synthesis of biologically active substances thermostable antioxidants for hydrocarbon fuels and lubricating oils, polymers and optical brighteners. A large class of derivatives is sim triazine compound a clearly defined antiprotozoal activity. The synthesis of these compounds and study their effects on various types of simple organisms is a major fields in modern chemistry triazine.

Triazine exhibiting antiprotozoal activity include tri-substituted sim-triazine containing halogen in an aromatic ring. General structural formula of the compounds is as follows the compounds is as follows

X = -O-, -CH₂ -
R = Hal, -OC(Hal)₃
R₁,R₂ = Alk
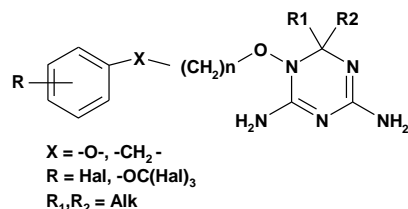
Recently hidrazo bis-1,3,5-triazine system has shown promise as a simple, stable, and inexpensive precursor for the synthesis of novel energetic materials. Synthetic work has resulted in several energetic compounds which have desirable properties.

II. Result and Discussion

We conducted the optimization of the reaction conditions. To optimize the nucleophilic substitution reaction has been used a number of solvents (DMSO, THF, acetonitrile, DMF), bases (K_2CO_3, Na_2CO_3), interactions were carried out at different temperatures and interaction time 2 hours. (Tabl. 1)

TABLE 1

Solvent	Base	T,°C	Time, h	Product yield, %
DMSO	K_2CO_3	100	2h	86
DMSO	Na_2CO_3	100	2h	80
DMSO	K_2CO_3	150	2h	75
DMSO	Na_2CO_3	150	2h	71
THF	K_2CO_3	60	2h	67
THF	Na_2CO_3	60	2h	59
Acetonitrile	K_2CO_3	80	2h	50
Acetonitrile	Na_2CO_3	80	2h	30
DMFA	K_2CO_3	100	2h	72
DMFA	Na_2CO_3	100	2h	64
DMFA	K_2CO_3	150	2h	65
DMFA	Na_2CO_3	150	2h	55
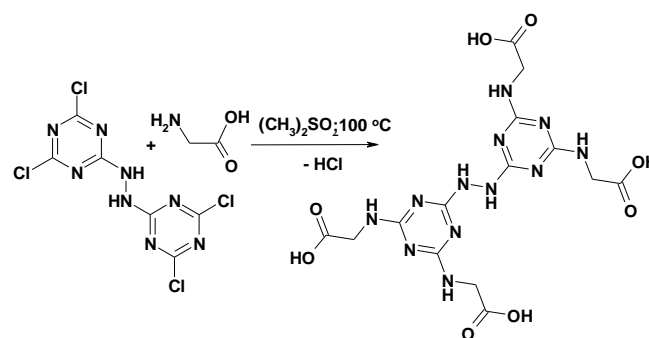
Depending on the reaction we received various outputs of the final product. It was found that during the interaction among DMSO in the presence of K_2CO_3 for 2 hours was recorded the best yield of the final product 4 (86%).

Studying interactions 4,6,4,6` hidrazo-tetrachloro-bis-1,3,5-triazine of glycine (Gly) at 100 °C in DMSO in the presence of K_2CO_3 for 2 hours showed that the reaction takes place to form N-products of nucleophilic substitution [4-{N'-[4,6-Bis-(carboxymethyl-amino)-

[1,3,5]triazin-2-yl]-hydrazino}-6-(carboxymethyl-amino)-[1,3,5]triazin-2-ylamino]-acetic acid - carboxylic acid 4 with 86% yield. This can be explained on the assumption that the mandatory component of the reaction and high product yield interaction is the presence of ionizing solvent (DMSO, DMF), which promotes the separation of the proton by a strong solvation.

Under conditions of ongoing optimization of the reaction was set the best conditions for further interactions 4,6,4`,6`hidrazo-tetrachloro-bis-1,3,5-triazine 1 of aliphatic amino acids and aminophosphonic acid.

Basics are directed synthesis of new heterocyclic systems based on hidrazo bis-1,3,5-triazine of phosphoric and amino acid fragments. The paper's task was to get a new heterocyclic system, as starting compounds for further design drugs based on these molecules.
As the original frame used 4,6,4`,6` hidrazo-tetrachloro-bis-1,3,5-triazine.
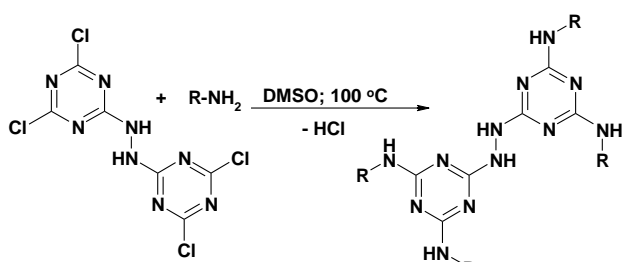
As the number of substitutes used aliphatic amino acids: glycine, methionine, threonine and (4-amino-1-hydroksybutyl) -1,1' diphosphonic acid.
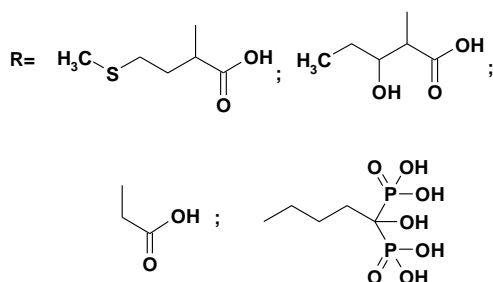
Conclusion

Hidrazo bis-triazine is an interesting reagent source for the construction of several new compounds that can be used as complexones.

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