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# **The Reticular Structure Characteristic of the Acrylonitrile Copolymers with Hexahydro - 1,3,5-Triakrililtriazinom**

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**ABSTRACT:** Research on improving methods for the synthesis of ion-exchange sorbents with a porous structure based on copolymers is relevant.

## **I. INTRODUCTION**

In this improved work, the results obtained by the new method are summarized. Obtaining a porous copolymer based on ion exchange sorbents is one of the current problems of today. The multifunctional group sewing agent hexahydro 1-3-5 with donor copolymer acrylonitrile was formed by ion exchange, and their swelling, densities, and some physical properties were studied. Polymers and materials based on them occupy a very important place in our life, their production is growing rapidly from year to year, new polymers are synthesized, are invented new materials. In this regard, the most important direction is the synthesis and ion-exchange materials structure study with desired properties, which are widely used in national economy various areas and that is important in ecology and environmental protection problems solving. Therefore, obtaining ion exchangers based on acrylonitrile by granular polymerization in the crosslinking agent presence with subsequent chemical modification of functional groups is urgent.

## **II. THE AIM OF THIS WORK**

Is to obtain granular ion exchange sorbents based on acrylonitrile copolymers with multifunctional crosslinking agent - hexahydro-1,3,5-triakrililtriazinom by their chemical transformations and the study of their network structure.

## **III. MAIN PART**

Acrylonitrile copolymers with crosslinking various structures agents have recently become the most common frameworks for the ion exchangers synthesis. They differ from different chemical composition scaffolds by the ability to control the crosslinking degree and availability for various chemical reactions.

Such polymers - ion exchangers have long been used in various sorption technologies that require special mechanical and chemical resistance, when it is necessary to concentrate technological solutions to extract especially valuable components from them, to purify water supply sources, industrial waste waters from toxic ions and environmentally hazardous compounds.

In this regard, studies to improve the ion-exchange sorbents synthesis methods with a porous structure based on the above and other copolymers are urgent.

This graduation work purpose is to obtain ion-exchange granular sorbents based on acrylonitrile copolymers with a multifunctional cross linking agent - hexahydro-1,3,5-triacrylyltriazine by their chemical transformations and their network structure study.

The physicochemical characteristics and sorption properties of the obtained copolymers depend on the macrochain structure, the functional groups nature of the obtained anionites, etc. However, the acrylonitrile copolymers network structure with hexahydro-1,3,5-triacrylyltriazine remained uncharacterized. Therefore, it was interesting to study the acrylonitrile copolymerization process with a cross linking agent hexahydro-1,3,5-triacrylyltriazine, which contains three vinyl groups in its structure.

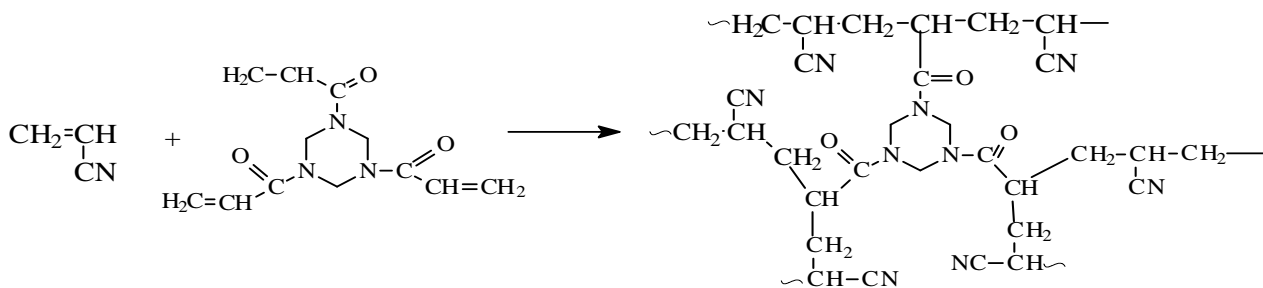
Copolymerization was carried out by the suspension method in the dinitrile-azo-isobutyric acid presence as an initiator (up to 1 wt% monomers mixture mass), stabilizer-water-soluble starch, at 343 K temperature in a NaCl (dispersion medium) saturated aqueous solution obtained at room temperature, at 450-500 rpm rotation speed; reaction time up to 5 hours.

The monomers ratio and blowing agent toluene, in which the initiator was dissolved and the dispersion medium was 1:4 (water modulus). To obtain a porous structure, an inert solvent toluene was used in 30% amount by monomer mixture weight. A 1% aqueous starch solution was used as a protective colloid. The required initiator amount, AN, HTT, stabilizer, blowing agent was introduced into a reactor equipped with a mechanical stirrer, refrigerator and previously placed in a thermostat with an initial temperature for copolymerization. After the reaction end, the reactor was removed from the thermostat and the samples were decanted.

As is known, suspension copolymerization takes place under heterophase conditions. Copolymerization takes place in monomer drops and the resulting copolymer is insoluble in its own monomer and in an aqueous-organic medium.

The granular copolymer does not dissolve in polyacrylonitrile solvents, which indicates the crosslinked structure presence.

The resulting copolymer structure between the reacting components can be schematically illustrated as follows:



Thus, a copolymer was obtained with the starting components: AN, HTT=97,5; 2,5; 97:3; 95:5 mass %.

**The copolymers density** was determined by the pycnometric method. To determine the copolymer density, at 293 K water density was studied for comparison with the copolymer density at the same temperature. After weighing the dry pycnometer with no more than 0.0002 g error, it was filled up to the mark with water, closed with a glass stopper, and immersed in a water bath with 293 K temperature for 30 min. After that, the water level in the pycnometer was accurately set to the mark.

After closing with a stopper and thoroughly wiping the pycnometer outside, a second weighing was performed. After that, water was poured out of the pycnometer, dried, cooled in a desiccator, and several pieces of the tested copolymer were placed. Closing the lid, a third weighing was carried out. Then the water level in the pycnometer was brought up to the mark, closed and immersed in a water bath with 293K for 30 min. Then the water level was brought to the mark, the water was carefully taken from the outside, and the fourth weighing was performed.

The copolymer density was determined by the formula:

$$\rho = \frac{m_2 - m_0}{(m_1 - m_0) - (m_3 - m_2)} \quad \text{where } m_0 \text{ - is pycnometer mass, g;}$$

$m_1$  - is the pycnometer weight with water, g;

$m_2$  - is pycnometer mass with copolymer, g;

$m_3$  - is pycnometer weight with water and copolymer, g;

**Copolymers swelling** - determined by gravimetric method. A weighed sample was placed in a weighing bottle containing 5 cm<sup>3</sup> of the corresponding liquid. The bottle was sealed, placed in a centrifuge, kept for 5 minutes at 3000 rpm speed, then taken out of the centrifuge, the bottle was freed from the sample with tweezers, and excess solvent was removed with filter paper and weighed on a balance with the 4th digit accuracy.

After weighing, the swollen sample was again placed in a bottle with solvent. The actions were repeated after 5, 10 and 15 minutes and further excerpts.

The measurements were stopped when the difference in the last three measurements masses did not exceed 3 mg.

The swelling degree for each time value was calculated using the following formula:

$$\alpha_{(\tau)} = \frac{m_{(\tau)} - m_0}{m_0}$$

where  $\alpha_{(\tau)}$  - the swelling degree of the sample for a fixed time value;

$m_{(\tau)}$  is the swollen sample mass for a fixed time value;

$m_0$  - is the starting material mass.

The swelling coefficient  $q_{2m}$  is calculated using the following formula:

$$q_{2m} = \frac{g_{2m} - g_2}{g_2} \cdot \frac{\rho_2}{\rho_0} + 1;$$

where  $g_2$ - is weighed amount of dry cross-linked polymer;  $g_{2m}$ - is the swollen cross-linked polymer sample;  $\rho_2$  and  $\rho_0$ - the polymer and solvent density, respectively. Index m indicates that this parameter is measured in an equilibrium swelling state. The samples swelling degree was studied by centrifugation.

Mesh parameters calculation

The number average molecular weight chain segments between cross linking sites ( $M_w$ ) and the chains concentration in the copolymer ( $n_c$ ), which characterize the crosslinking density, were calculated using the equation proposed in [39]:

$$M_c = \frac{\rho_2 V_1 \left[ (q_{2m} + 1)^{-\frac{1}{3}} - \frac{1}{2} (q_{2m} + 1)^{-1} \right]}{\ln \left( \frac{1}{q_{2m} + 1} \right) - (q_{2m} + 1)^{-1} - \chi_1 (q_{2m} + 1)^{-2}}$$

where  $\rho_2$  is polymer density;  $q_{2m}$  is swelling constant;  $V_1$  is solvent molar volume;  $\chi_1$  is Huggins parameter (for the polyacryloniril- DMF (Dimethylformamide) system is taken equal to 0.29).

The grid parameters were calculated using the found the number average molecular weight values ( $M_w$ ) of the active chain and the polymer density according to the following formula:

$$n_c = \frac{N_c}{N_A} = \frac{\rho_2}{M_c} = \frac{v_c}{V_c} = \frac{1}{V_2}$$

where  $v_c$  is moles number of active chains in the sample, moles;  $n_c$  is the moles number of active chains per unit volume of the cross-linked copolymer, moles/cm<sup>3</sup>;  $N_c$  is the concentration of active chains per unit volume of the cross-linked polymer (cm<sup>3</sup>)<sup>-1</sup>;  $N_A$  is Avogadro's number;  $\overline{V_c}$  is the effective molar volume of the active chain, cm<sup>3</sup>/moles;  $V_2$  - polymer volume, cm<sup>3</sup>.



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