IMPROVEMENT BY THE METHOD OF SYNTHESIS OF ION-EXCHANGE SORBENTS

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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. 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.

Keywords: sorbent, acrylonitrile, network structure, copolymer, granule, monomer, stabilizer, density, swelling, crosslinking agent.

INTRODUCTION

The aim of this work is to obtain ion-exchange granular sorbents based on copolymers of acrylonitrile with a multifunctional crosslinking agent - hexahydro-1, 3,5-triacrylyltriazine by their chemical transformations and to study their network structure. 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, and new materials are invented. In this regard, the most important direction is the synthesis and study of the structure of ion-exchange materials with desired properties, which are widely used in various fields of the national economy and which is important in solving problems of ecology and environmental protection. Therefore, obtaining ion exchangers based on acrylonitrile by granular polymerization in the presence of a crosslinking agent with subsequent chemical modification of functional groups is urgent [1].

Copolymers of acrylonitrile with crosslinking agents of various structures have recently become the most common scaffolds for the synthesis of ion exchangers. They differ from frameworks of other chemical composition in the ability to control the degree of crosslinking and accessibility 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 water from toxic ions and environmentally hazardous compounds [2].

In this regard, studies on the improvement of methods for the synthesis of ion-exchange sorbents with a porous structure based on the above and other copolymers are relevant.

The purpose of this graduate work is to obtain ion-exchange granular sorbents based on copolymers of acrylonitrile with a multifunctional crosslinking agent - hexahydro-1, 3, 5-triacrylyltriazine by their chemical transformations and the study of their network structure.

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

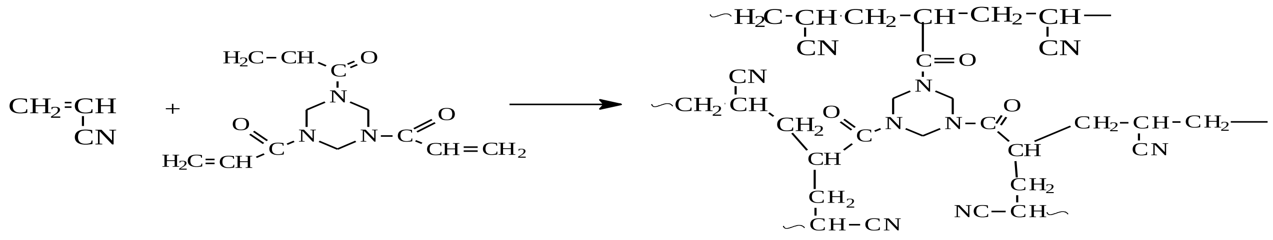
Copolymerization was carried out by the suspension method in the presence of dinitrile-azo-isobutyric acid as an initiator (up to 1 mass% of the mass of the mixture of monomers), stabilizer-water-soluble starch, at a temperature of 343 K in a saturated aqueous solution of NaCl (dispersion medium) obtained at room temperature. Temperature, at a rotation speed of 450-500 rpm; reaction time up to 5 hours [3].

The ratio of monomers 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 an amount of 30% by weight of the mixture of monomers. A 1% aqueous starch solution was used as a protective colloid. The required amount of initiator, AN, GTT, stabilizer, blowing agent was introduced into a reactor equipped with a mechanical stirrer, a refrigerator and previously placed in a thermostat with an initial temperature for copolymerization. After the end of the reaction, the reactor was removed from the thermostat and the samples were decanted [4].

As is known, suspension copolymerization takes place under heterophase conditions. Copolymerization takes place in drops of monomer 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 presence of a crosslinked structure.

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



Thus, a copolymer was obtained with the starting components: AN: GTT = 97.5: 2.5; 97: 3; 95: 5 wt%.

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

After closing with a plug and thoroughly wiping the outside of the pycnometer, 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, the 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 carried out.

The density of the copolymer was determined by the formula:

$$\rho = \frac{m_2 - m_0}{(m_1 - m_0) - (m_3 - m_2)}$$

Where is the mass of the pycnometer, g;
- Mass of the pycnometer with water, g;
- Mass of the pycnometer with copolymer, g;
- Mass of the pycnometer with water and copolymer, g;

SWELLING OF COPOLYMERS

Determined by gravimetric method. A weighed portion of the sample was placed in a weighing bottle containing 5 cm3 of the corresponding liquid. The bottle was sealed, placed in a centrifuge, kept for 5 minutes at a speed of 3000 rpm, then removed from 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 an accuracy of the 4th digit.

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 masses of the last three measurements did not exceed 3 mg.

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

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

Where is the degree of swelling of the sample for a fixed time value?
Is the mass of the swollen sample for a fixed time value?
Is the mass of the starting material?
The swelling coefficient q2m was 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 a sample of dry cross-linked polymer; g 2m-weight of the swollen cross-linked polymer; (2 and (0 are the density of the polymer and solvent, respectively. The index m indicates that this parameter was measured in the state of equilibrium swelling. The degree of swelling of the samples was studied by the centrifugation method.

Calculation of mesh parameters

The number average molecular weight of chain segments between crosslinking sites (ML) and the concentration of chains in the copolymer (nC), which characterize the crosslinking density, were calculated using the equation proposed in [39]:

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

Where, ρ_2 -is the density of the polymer; q_{2m} - swelling constant; V_1 - the molar volume of the solvent; χ_1 - Huggins parameter (for the polyacryloniril-DMF system it is taken equal to 0.29).

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

$$n_C = \frac{N_C}{N_A} = \frac{\rho_2}{M_C} = \frac{\nu_C}{\overline{V_C}} = \frac{1}{V_2}$$

where, ν_C -is the number of moles of active chains in the sample, mol; n_C - the number of moles of active chains per unit volume of the crosslinked copolymer, mol / cm^3; N_C - concentration of active chains per unit volume of cross-linked polymer (cm^3)$^{-1}$; N_A - Avogadro's number; $\overline{V_C}$ - effective molar volume of the active chain, cm^3/mol; V_2 - polymer volume, cm^3.

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