Volume 3, Issue 11, November - 2025
ISSN (E): 2938-3781

STRUCTURE OF ACRYLONITRILE AND HEXAHYDRO-1,3,5-TRIACRYLYLTRIAZINE SOPOLYMER

Prof. Kh. Dj. Ismoilova
Karshi State Technical University

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.

Introduction

Polymers and materials based on them occupy a very important place in our lives, their production increases at a rapid pace 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 specified 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, the production of acrylonitrile-based ion exchangers by granular polymerization in the presence of a cross-linking agent followed by chemical modification of functional groups is relevant.

Copolymers of acrylonitrile with cross-linking agents of various structures have recently become the most common frameworks for the synthesis of ion exchangers. They differ from scaffolds of other chemical compositions in their ability to control the degree of cross-linking and their 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 supplies and industrial wastewater from toxic ions and environmentally hazardous compounds. In this regard, research to improve methods for the synthesis of ion-exchange sorbents with a porous structure based on the above and other copolymers is relevant.

The purpose of this graduation work is to obtain ion-exchange granular sorbents based on copolymers of acrylonitrile with a multifunctional cross-linking agent - hexahydro-1,3,5-triacrylyltriazine through their chemical transformations and study 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 anion exchangers, etc. But the network structure of acrylonitrile copolymers with hexahydro-1,3,5-triacrylyltriazine remains uncharacterized. Therefore, it was interesting to study the process of copolymerization of acrylonitrile with the cross-linking agent hexahydro-1,3,5-triacrylyltriazine, which contains three vinyl groups in its structure.

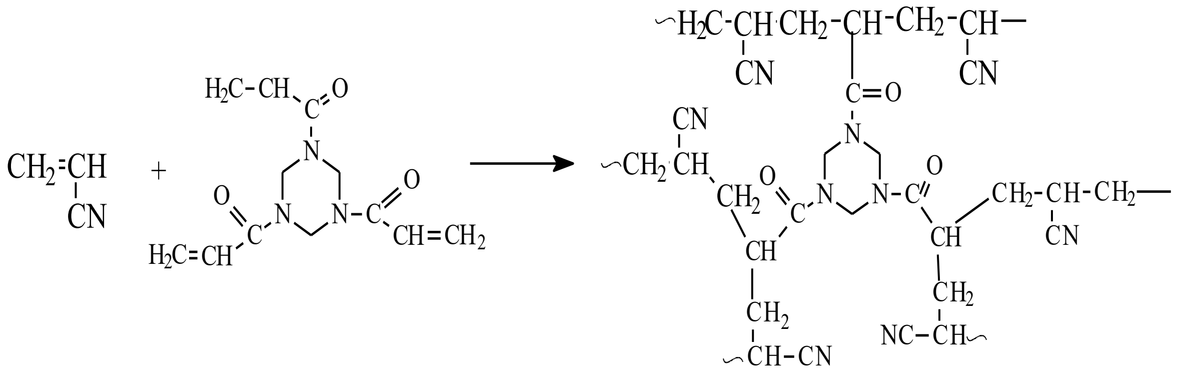
Copolymerization was carried out by the suspension method in the presence of dinitrile-azo-isobutyric acid as an initiator (up to 1 wt.% by weight of the mixture of monomers), stabilizer-water-soluble starch, at a temperature of 343 K in a saturated aqueous solution of NaCl (dispersion medium), obtained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

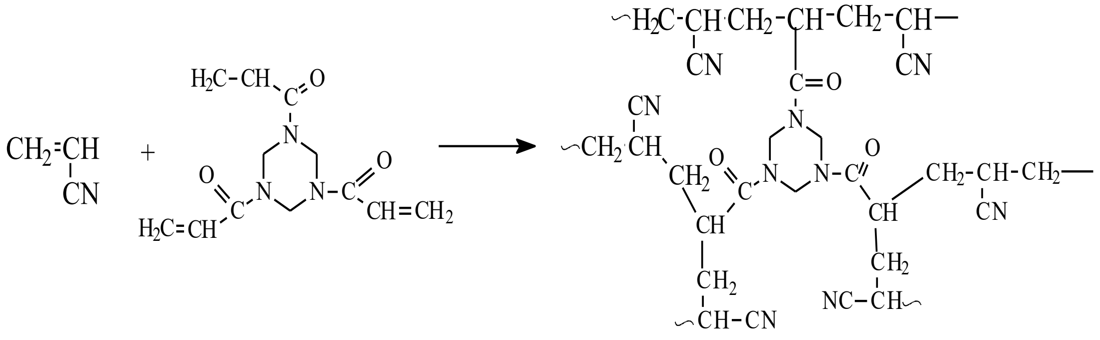
The ratio of monomers and pore-forming agent toluene, in which the initiator was dissolved and the dispersion medium was 1:4 (aqueous module). To obtain a porous structure, the inert solvent toluene was used in an amount of 30% by weight of the mixture of monomers. A 1% aqueous solution of starch was used as a protective colloid. A 1% aqueous solution of starch was used as a protective colloid. The required amount of initiator, AN, GTT, stabilizer, pore former 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 reaction was completed, the reactor was removed from the thermostat and the samples were decanted.

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

The granular copolymer is insoluble in polyacrylonitrile solvents, which indicates the presence of a cross-linked structure.

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





Thus, a copolymer was obtained with the original components: AN:GTT = 97.5: 2.5; 97:3; 95:5 wt %. The density of copolymers was determined by the pycnometric method. To determine the density of the copolymer, the density of water at 293 K was studied for comparison with the density of the copolymer at the same temperature.

The density of copolymers was determined by the pycnometric method. To determine the density of the copolymer, the density of water at 293 K 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, fill it to the mark with water, close it with a glass stopper and immerse it in a water bath with a temperature of 293 K for 30 minutes. After this, the water level in the pycnometerwas accurately adjusted to the mark.

Then the water level was brought to the mark, water was carefully taken from outside and the fourth weighing was performed.

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:

m_0 - mass of the pycnometer, g;
m_1 - mass of the pycnometer with water, g;
m_2 - mass of pycnometer with copolymer, g;
m_3 - mass of the pycnometer with water and copolymer, g;

The swelling of copolymers was determined by the gravimetric method. A sample samplewas placed in a bottle containing 5 cm^3 of the corresponding liquid. The bottle was hermetically 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 using tweezers, excess solvent was removed with filter paper and weighed on a scale with an accuracy of the 4th digit.

After weighing, the swollen sample was again placed in a bottle with a 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 $\alpha_{(\tau)}$ - is the degree of swelling of the sample for a fixed time value;
m1 - mass of the swollen sample for a fixed time value;
m2 - mass of the starting substance.

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 the sample of dry cross-linked polymer;
g_{2m} - sample of swollen cross-linked polymer;
ρ_{2}- and p_0 - are the densities of the polymer and solvent, respectively.

The index m indicates that this parameter was measured in a state of equilibrium swelling. The degree of swelling of the samples was studied by centrifugation.

Calculation of mesh parameters. The number-average molecular weight of chain segments between cross-linking sites (MC) and the concentration of chains in the copolymer (nC), characterizing the cross-linking 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 polymer density;

q_{2m} - swelling constant;

V_1 - molar volume of solvent;

χ_1 - Huggins parameter (for the polyacrylonitrile
ДМФА- system it is assumed to be 0.29).

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

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

Where ν_C - is the number of moles of active chains in the sample, mol;

n_C - number of moles of active chains per unit volume of cross-linked copolymer, mol/cm^3;

N_C - concentration of active chains per unit volume of cross-linked polymer (cm^3);

N_A - Avogadro's number;

$\overline{V}_C$ - effective molar volume of the active chain, cm^3/mol; - polymer volume, cm^3.

References

1. Иониты и ионный обмен. Сборник статей под ред. Самсонова Г.В., Л, Наука, 1975, с. 5-10.
2. Сайдл М., Мамински Я., Душек К., Ионообменные каркасы с пористой структурой на основе сополимеров стирола с дивинилбензолом. Пластмассы, 1963, № 12с. 7.
3. Энциклопедия полимеров. М, С.Э., т 1, с 998.
4. Пат. 96740 СРР, МКИ^{4}С 08 F 12/36, C 08 F 20/26. Способ получения сшитого сополимера с пористой структурой/Поинеску П.И. (ЧССР).- №54-10357;Заявл. 25.12.65;Опубл. 4.05.79.

4\. Ли Я., Шенг Ф. Синтез и изучение сетчатых хелатных полимеров на основе акрилонитрила. II. Изучение с помощью ИК-спектроскопии сетчатых полимеров на основе акрилонитрила.//Actapolym. Sci.-1990. -№5. -С.618-622.

5. ЙокотаКадзуаки, ТоминагаМакото, ТакатаЙосиюки. Сополимеризация акрилонитрила с β-стиролсульфонатом натрия и β-стиролсулфонамидом.// Хоккайдо дайгакукогакубукэнкюхококу, Bull.Fac.Eng.HokkaidoUniv. -1968. -№47. -С.131-140.
6. Трубицина С.И., Исмаилов И., Аскаров М.А. Сополимеризация акрилонитрила с рядом мономеров под действием инициирующей системы азотсодержащий мономер-персульфат калия.// Высокомолек.соед. -1977. -А19. -№3. -С.495-499.
7. Исмаилова Х. Дж. Органическая химия. Учебник для высших учебных заведений. 2022 год.