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SYNTHESIS OF CROSS-LINKED ACRYLONITRILE COPOLYMER WITH HEXAHYDRO-1,3,5-TRIACRYLYLTRIAZINE BY SUSPENSION COPOLYMERIZATION

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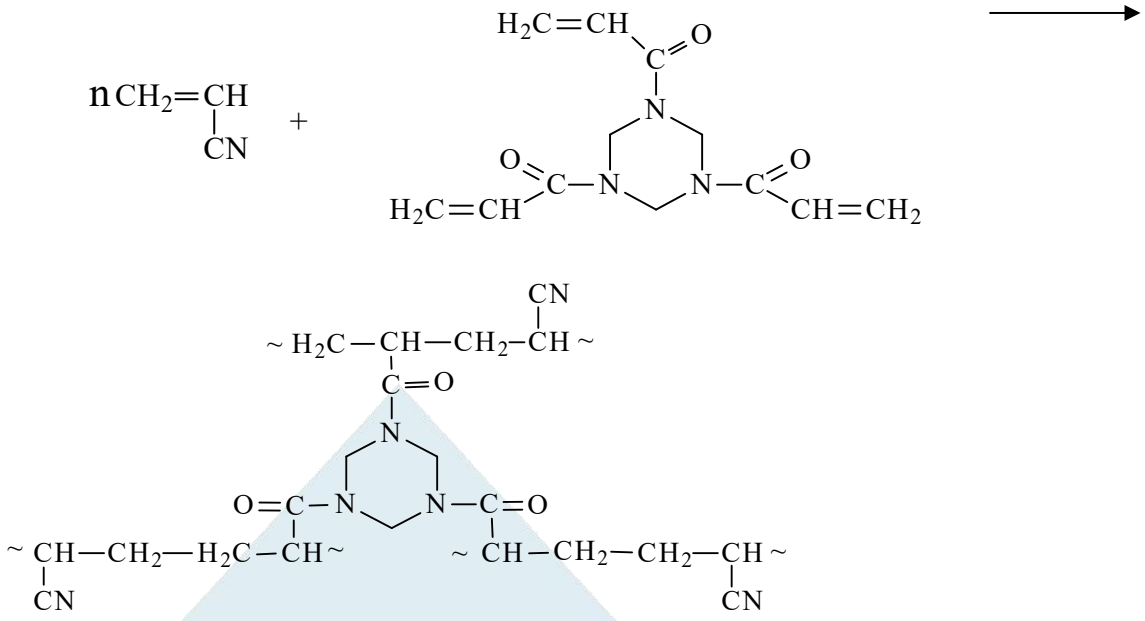
Annotation: The choice of acrylonitrile as the main precursor for obtaining a polymer matrix is dictated by economic reasons. Acrylonitrile is an industrially available monomer produced by Navoiazot JSC. However, due to changes in the world market conditions and increased competition from foreign manufacturers of polyacrylonitrile materials, Navoiazot JSC is currently experiencing enormous difficulties in selling its products to foreign markets.
Keywords: Acrylonitrile, hexahydro 1,3,5-triacrylyltriazine, reaction kinetics.

Introduction. The kinetic features of the copolymerization of acrylonitrile in the presence of divinylbenzene (DVB) and N,N'-methylene-bis-acrylamide are known in the literature [1]. However, the regularities of AN copolymerization in the presence of HTT have not been studied. In connection with this, the influence of various factors on the process of suspension copolymerization of AN with HTT was studied. It should be noted that the study of the influence of various factors (reaction time, system temperature, ratio of initial monomers, etc.) on the nature of copolymerization is important for targeted regulation of the physicochemical properties of the resulting product [2].

The copolymerization reaction of AN with HTT can be represented schematically as follows:



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The obtained granular copolymer does not dissolve in the solvent for polyacrylonitrile - dimethylformamide, which indicates the formation of a polymer with a three-dimensional cross-linked structure.

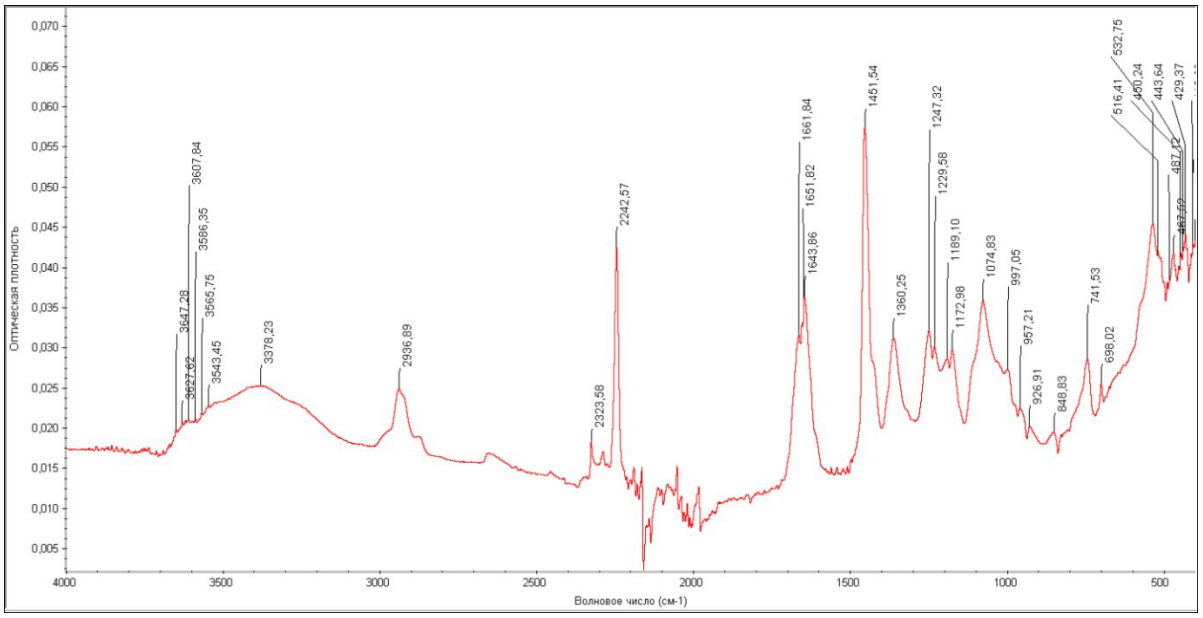

Fig.1. Fourier IR spectrum of the AN-HTT copolymer.

Fourier IR spectroscopy was used to identify the resulting copolymer. Figure 1 shows the Fourier IR spectra of the initial HTT and the obtained cross-linked copolymer of AN with HTT. In the IR spectrum of the copolymer, the following absorption frequencies were found: 2240 cm-1 - stretching vibrations of the nitrile group (ν_{CN}), 1647 cm-1 - stretching vibration of the carboxyl amide group (νC=O), 1445 cm-1 - bending vibration of the CH2 - group (νCH2) [3].

Figure 2 shows the dependence of the duration of the copolymerization reaction on the yield of granulated AN-HTT copolymer. As can be seen from the data presented in Fig. 2, the dependence curve does not have a segment characteristic of the induction period, which is observed in the case of copolymerization of AN with MBA [4]. Unlike the AN-MBA copolymerization process, which has an S-shape and indicates self-acceleration of the process, the AN-HTT copolymerization proceeds intensively in the time interval of 0-1.5 hours. Further, the process slows down and at 2.0 h equilibrium is reached in the system and the yield of the granulated copolymer remains unchanged [5].

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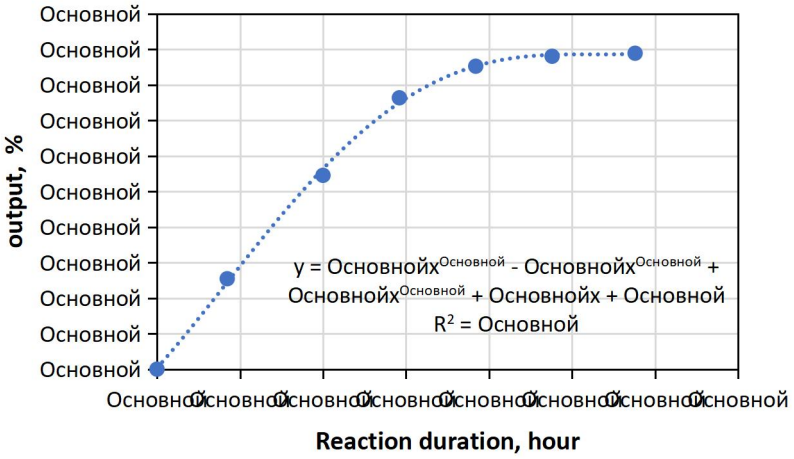

Fig.2. Dependence of the yield of AN-HTT granulated copolymer on the duration of the copolymerization reaction. [AN]:[HTT]=95.0:5.0 mol.%, T = 343 K, Vdisp=400-450 rpm, [I]=1 wt.%, [Toluene]=30 wt. %, BM=1:4.

It was interesting to investigate the effect of the amount of HTT crosslinking agent on the yield of AN-HTT granular copolymer. Figure 3 shows the dependence of the yield of AN-HTT granular copolymer on the amount of cross-linking agent (HTT) in the initial mixture of monomers.

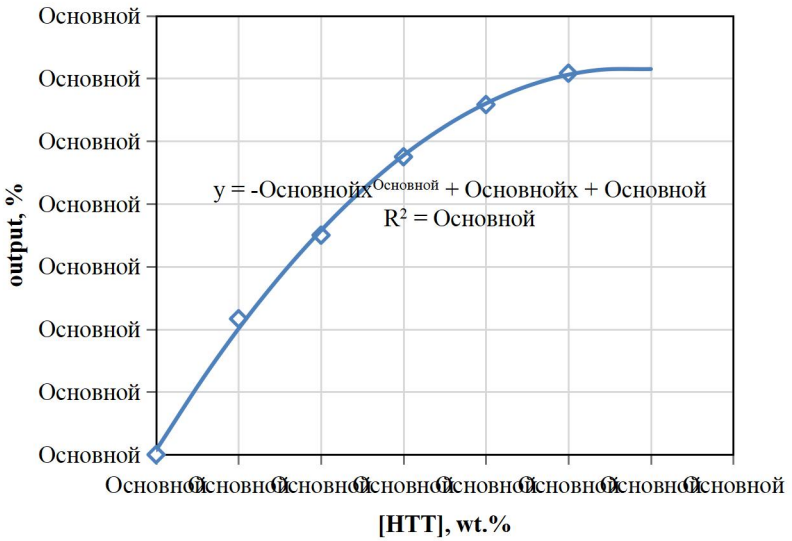

Fig.3. Dependence of the yield of AN-HTT granulated copolymer on the amount of cross-linking agent (HTT) in the initial mixture of monomers. Reaction time, τ=1 hour, T=343 K, V_{disp}=400-450 rpm, [I]=1 wt.%, [Toluene]=30 wt. %, BM=1:4.

It can be seen from the data presented in Fig. 3 that the yield of the copolymer strongly depends on the initial composition of the mixture of monomers, and with a change in the content of HTT in the mixture from 1.0 to 6.0 mol%, an increase in the yield of granular copolymer from

25.5% to 89.9 %, respectively [6]. This indicates that HTT paired with AN has a markedly higher reactivity, which is probably due to the presence of three unsaturated bonds.

Conclusion. The comparative advantages of the suspension polymerization method are shown as the most effective method in terms of controlling the composition, spatial structure, and physic-mechanical properties of the obtained polymers depending on the conditions of their operation in various fields.

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