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

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Annotation

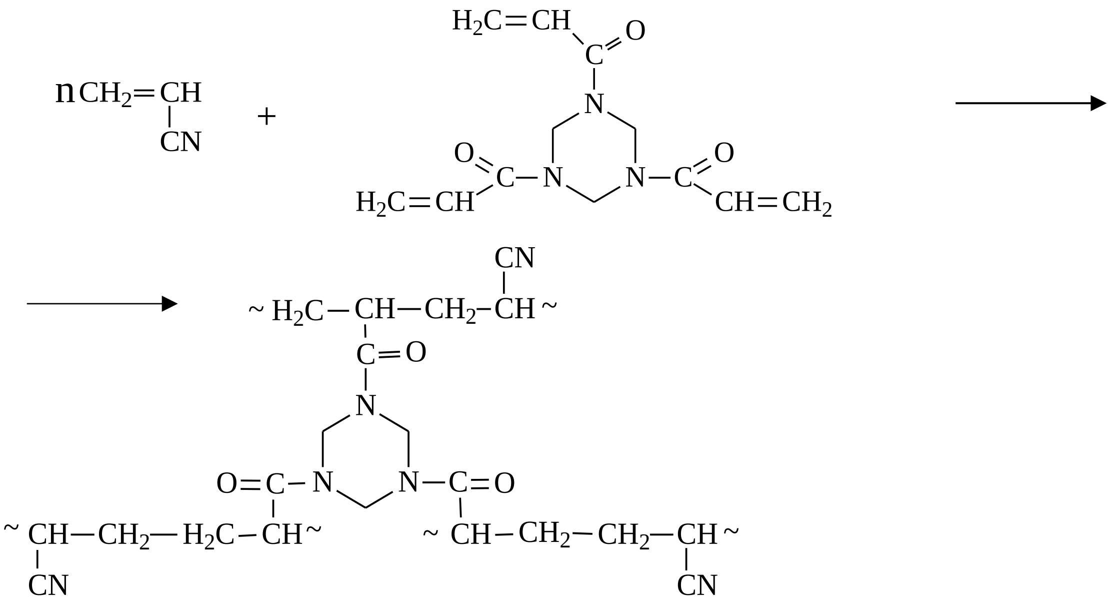
The choice of acrylonitrile as the main precursor for the production of the polymer matrix is dictated by economic reasons. Acrylonitrile is an industrially available monomer, which is produced by Navoiazot JSC. However, due to changes in the world market and increased competition from foreign manufacturers of polyacrylonitrile materials, Navoiazot JSC is currently experiencing enormous difficulties in selling its products to foreign markets.

Keywords: monomer, cross-linking agent, andcrylonitrile, hexahydro- 1,3,5-triacrylyl triazine, copolymerization, reaction kinetics, sorbents.

The kinetic features of the copolymerization process of acrylonitrile (AN) in the presence of divinylbenzene (DVB) and N,N'-methylene-bis-acrylamide are known in the literature [1]. However, the regularities of copolymerization of AN in the presence of hexahydro-1,3,5-triacrylyl triazine (GTT) have not been studied . In this regard, the influence of various factors on the process of suspension copolymerization of AN with GTT was investigated. It should be noted that the study of the influence of various factors (reaction duration, system temperature, ratio of initial monomers, etc.) on the nature of copolymerization is important for the targeted regulation of the physicochemical properties of the resulting product [2]. The resulting granular copolymer is insoluble in the solvent for polyacrylonitrile - dimethylformamide, which indicates the formation of a polymer with a three-dimensional cross-linked structure.

Fourier IR spectroscopy was used to identify the resulting copolymer. Fig.1 shows the Fourier IR spectrum of the obtained cross-linked copolymer of AN with GTT. The following absorption frequencies were found in the IR spectrum of the copolymer: 2240 cm-1 – valence oscillations, valence oscillation of the nitrile group ($C_{N}\nu$), 1647 cm-1 – carboxyl of the amide group ($_{C\,=\,O}$), 1445 ν^{cm-1} – deformation oscillation of CH_2 – group (δ_{CH_2}) [3].

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



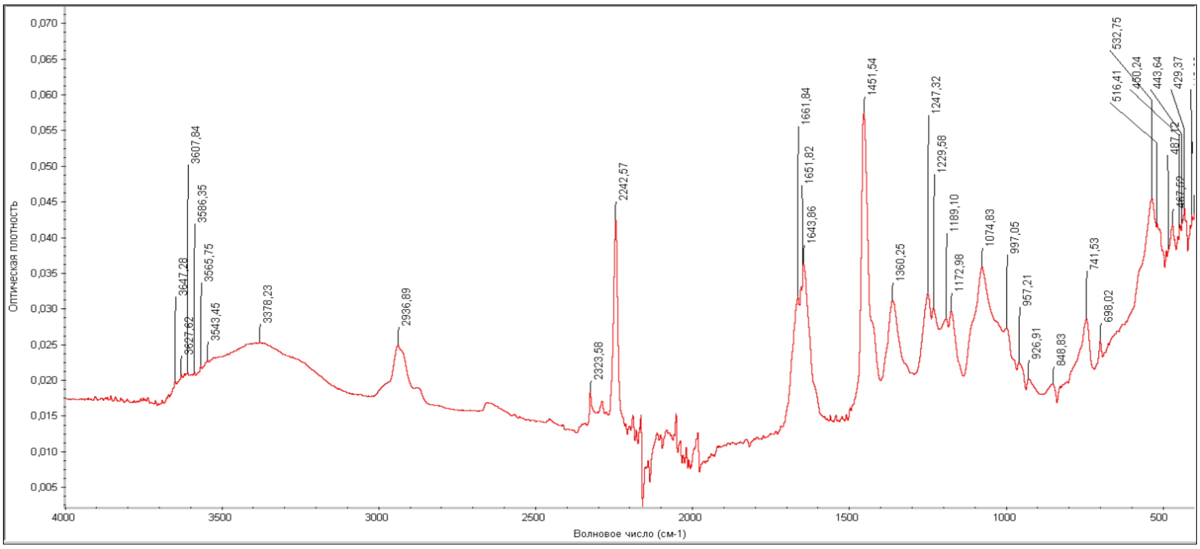


Fig.1. Fourier IR spectrum of AN-GTT copolymer.

Fig.2 shows the dependence of the duration of the copolymerization reaction on the yield of granular copolymer AN-GTT. As can be seen from the data presented in Fig.2, the dependence curve does not have a characteristic section for the induction period, which is observed in the case of copolymerization of AN with MBA [4]. In contrast to the AN-MBA copolymerization process,which has an S-shape and indicates the self-determination of the process, the copolymerization of AN-GTT proceeds intensively in a time interval of 0-1.5 hours. In the future, there is a slowdown in the process at 2.0 hours. equilibrium is achieved in the system and the yield of the granular copolymer remains unchanged [5].

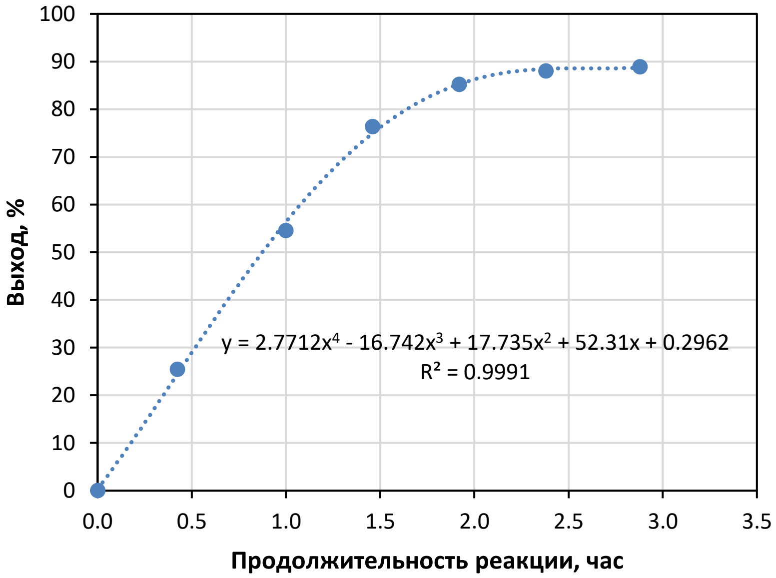


Fig.2. Dependence of the yield of granular copolymer AN-GTT on the duration of the copolymerization reaction. [AN]:[GTT]=95.0:5.0 mol. %, T = 343 K, V_{per} = 400-450 rpm, [I] = 1 wt.%, [toluol] = 30 wt. %, BM = 1: 4.

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

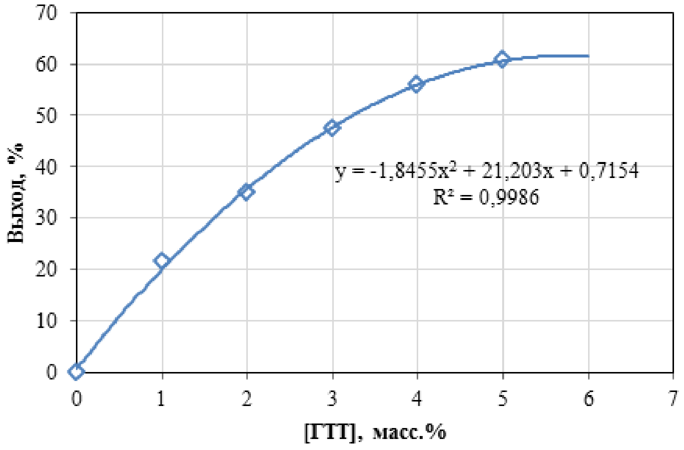
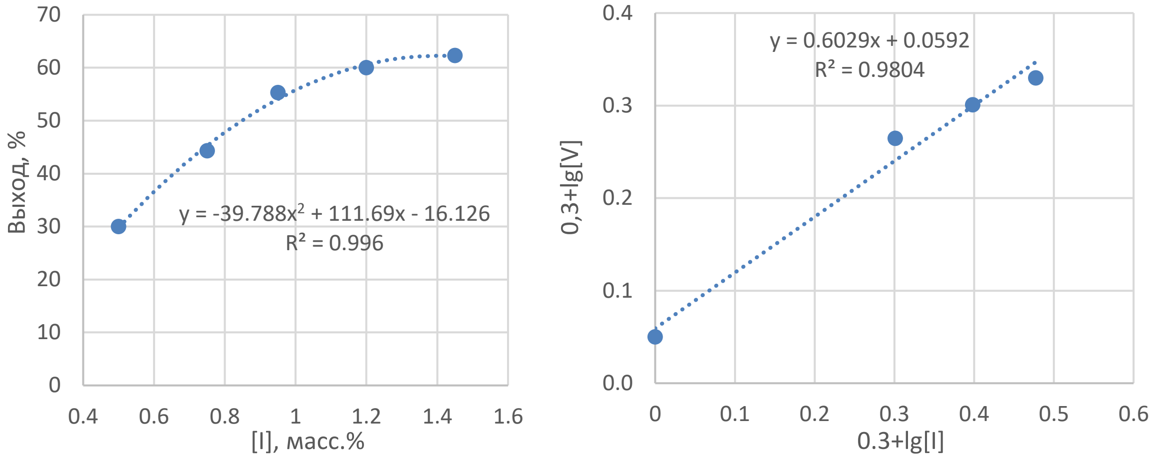


Fig.3. Dependence of the yield of granular copolymer AN-GTT on the amount of cross-linking agent (GTT) in the initial mixture of monomers. Duration of the reaction,

τ=1 час, T = 343 K, $V_{пер}$=400-450 об/мин, [I]=1 масс.%, [толуол]=30 масс. %, ВМ=1:4.

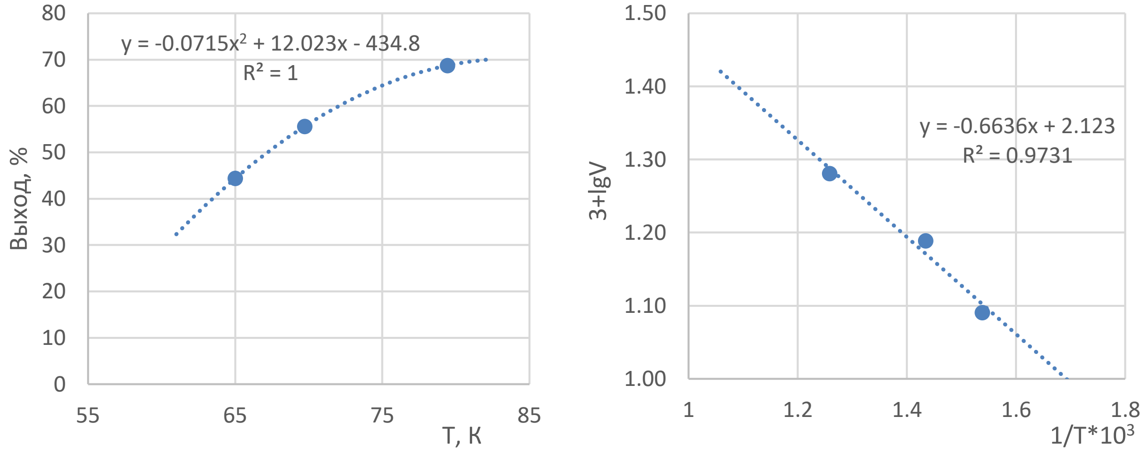
As can be seen from Fig.3, the yield of the copolymer strongly depends on the initial composition of the mixture of monomers and when the content of GTT changes from 1.0 to 6.0 moles, there is an increase in the yield of the granular copolymer from 25.5% to 89.9%, respectively, which indicates that GTT paired with AN has a noticeably higher reactivity, which is probably due to thepresence of three unsaturated bonds [6].

The effect of the initiator concentration on the conversion of monomers into a copolymer of AN with GTT was studied at 343 K for 1 hour, with a ratio of monomers of 95.0:5.0 mol. % and to the concentrationand initiator in the range of 0.5-1.45 wt. %. As can be seen from Fig. 4, the yield of the granular copolymer increases from 30.0 to 62.3 % with the studied initiator concentration interval. From the logarithmic dependence of velocity copolymerization from the concentration of DAC (Fig. 4) found the order of the reaction by the concentration of the initiator, which is equal to 0.6, which corresponds to the laws of radical heterogeneous polymerization.



Rice. 4. Dependence of the yield of granular copolymer AN–GTT on the concentration of the initiator at = 1 hour, τT = 343 K, V_{per} = 400-450 rpm, [I] = 1 wt. %,   [t oluol] = 30 wt. %, BM = 1: 4.

These data are confirmed by the results of studying the dependence of the effect of temperature on the process of copolymerization of AN with GTT in the temperature range 338-352K, presented in Fig. 5. It was found that the yield of the copolymer increases with increasing reaction temperature (Fig. 5). The value of the total activation energy of copolymerization [7], calculated on the basis of the logarithmic dependence of the polymerization rate on the inverse temperature value (Fig. 5) is 28.9 kJ/mol. The relatively low value of the activation energy may be due to the activity of the multifunctional monomer GTT.



Rice. 5. Dependence of the yield of the granular copolymer AN–GTT on the temperature (a) and on the reverse temperature of the reaction at = 1 hour, τV_{per} = 400-450 rpm, [I] = 1 wt. %, [t oluene] = 30 wt. %, BM = 1: 4.

Conclusion

The comparative advantages of the suspension polymerization method as the most effective method in terms of regulating the composition, spatial structure and physical and mechanical properties of the resulting polymers, depending on the conditions of their operation in various fields, are shown.

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