Preparation of Polyacrylamide by Hydrolysis of Acrylonitrile

Makhkamova L.K.	Assistant, Tashkent State Technical University
Maksumova O.S.	Professor, Tashkent Institute of Chemical Technology

ABSTRACT

The most important nitrile used in industry is acrylonitrile. In the petrochemical and oil-producing industries, materials obtained on its basis are actively used. First of all, these are polyacrylonitrile fibers, acrylonitrile – butadiene – styrene resins and other plastic materials with such unique properties as high benzo, oil, frost resistance and others.

Keywords: acrylamide, hydrolysis, polymers, sulfuric acid.

The paper analyzes ways to reduce costs in the production of poly [acrylonitrile (AN)–co–methylacrylate (MA)–co–2-acrylamide-2-methylpropanesulfonic acid (AMPS)]. The process of homophase free radical synthesis of these fiber-forming copolymers of acrylonitrile in dimethylformamide (DMF) is considered. To study the dynamics of the homophase synthesis of poly [AN–so–MA–so–AMPS], a pilot bench installation was created, which made it possible to simulate the influence of various factors (parameters) on the course of this process. It is shown that the increase in the water content in the reaction medium from 0.3 to 3.6% (wt.) it does not have a negative effect on the dynamics of the synthesis of these copolymers, as well as on the physical and mechanical properties of the fibers obtained on their basis. It is shown that in order to reduce the cost of solvent regeneration, the water content in the regenerated DMF can be increased from 0.05 to 1.00% (wt.) [1].

In this article, the authors considered one of the newest methods for obtaining a known monomer – acrylamide, justified the optimal conditions for the reaction, the use of acrylamide in various industries in compliance with environmental friendliness and a multi-percent yield of the product of further polymerization [2]. The greatest interest for the synthesis of acrylamide is the hydrolysis reaction from acrylonitrile.

$$CH_2{=}CHCN + H_2O \rightarrow CH_2{=}CHCONH_2$$

Previously, this process was carried out with 80-85% sulfuric acid, which led to excessive consumption of reagents and the formation of ammonium sulfate waste according to the following scheme:

$$CH_2{=}CHCN{+}H_2O{+}H_2SO_4 \rightarrow CH_2{=}CHCONH_2{\cdot}H_2SO_4$$

$$+2NH_3 \rightarrow CH_2{=}CHCONH_2 + (NH_4)_2SO_4$$

In addition, a side reaction occurs with the formation of a small amount of acrylic acid:

$$CH_2{=}CHCN + 2H_2O + H_2SO_4 \longrightarrow CH_2{=}CHCOOH + NH_4HSO_4$$

Later it was discovered that metallic copper is an effective catalyst. Synthesis is carried out in an aqueous solution at 70-1200C; copper is filtered out of the reaction mass and the unconverted acrylonitrile is distilled, recirculating them into the reactor. An aqueous solution of acrylamide is evaporated to a concentration of 30-50% or until crystalline acrylamide is obtained [3].

Acrylamide easily polymerizes into water-soluble polyacrylamide, which is a valuable flocculant widely used for the separation of aqueous suspensions, during flotation, wastewater treatment, etc.

In this section, the hydrolysis reaction of acrylonitrile with 98% sulfuric acid in the presence of an initiator was carried out. Benzoyl peroxide (PB) was used as the initiator. In the presence of sulfuric acid and the initiator of BP, the simultaneous participation of AN in the hydrolysis reaction with the formation of acrylamide and polymerization of the latter in the presence of BP is possible. After the reaction of AN hydrolysis, acrylamide (AA) is formed in the reaction mixture and its joint polymerization begins. The general reaction of hydrolysis and polymerization can be described by the following scheme:

$$CH_2{=}CHCN + H_2SO_4 \rightarrow nCH_2{=}CHCONH_2 \rightarrow -(CH_2{-}CHCONH_2)_n-$$

Kinetic studies of the process were investigated by the ampoule method. In the presence of sulfuric acid and the initiator of PB, the reaction consisted of hydrolysis and polymerization. In the absence of an initiator, the measured values related only to the hydrolysis reaction. At the same time, a gradual decrease in the reaction rate (V) was observed due to the consumption of acrylonitrile. In the presence of the initiator of the PB, the reaction rate increased, then it began to decrease. This phenomenon can confirm the simultaneous course of hydrolysis and polymerization reactions. Apparently, the chain growth reaction proceeds at a higher rate, which leads to an increase in the polymerization rate as the reaction proceeds, despite the consumption of the monomer.

The influence of various parameters on the course of the reaction was studied: concentrations of reagents, temperature, reaction duration on the yield of the product.

It was found that with an increase in the concentration of sulfuric acid, the rate of hydrolysis of AN with the formation of AA increases, and the rate of polymerization reaction decreases (Fig.3).

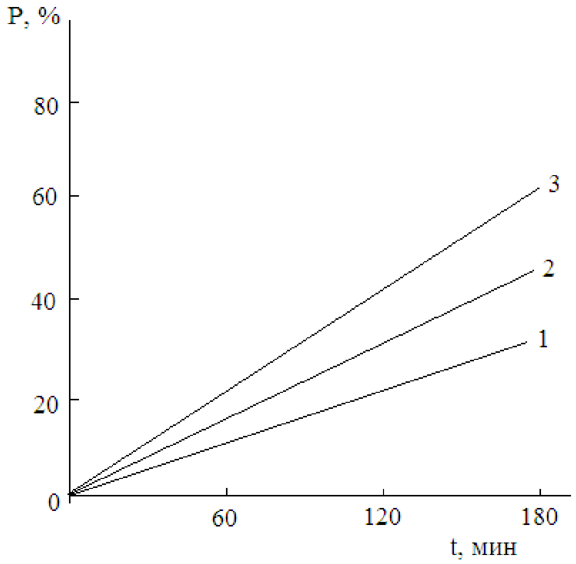

Fig.3 Dependence of the yield of AA on the concentration of sulfuric acid, %: 1- 75; 2-78; 3-80. [AN]=1 mol/l, [PB]=1%, 60 ^{o}C.

Experiments have shown that the concentration of aqueous solutions of H2SO4 also affects the solubility of the resulting product. It has been established that there is a rather narrow range of acid concentrations when the polymer has water solubility. The width of this range depends on the initial concentration of AN and narrows as it increases.

It is established that when the concentration of sulfuric acid increases to 98%, an insoluble solid precipitate is formed. The optimal ratio between the rates of hydrolysis and polymerization can be achieved not only by changing the concentration of sulfuric acid, but also the initiator- benzoyl peroxide. Its effect on the speed of the process turned out to be rather weak (the order of the reaction according to the initiation rate is 0.30). The detected deviations from the ideal kinetics are due to the simultaneous course of polymerization and hydrolysis of acrylonitrile, as a result of which a more polymerizationally capable monomer, acrylamide, is formed. The effect of the initiator concentration on the water solubility of polyacrylamide has been studied. It was found that with an increase in the initiator concentration, the water solubility of polyacrylamide improves (Fig.4).

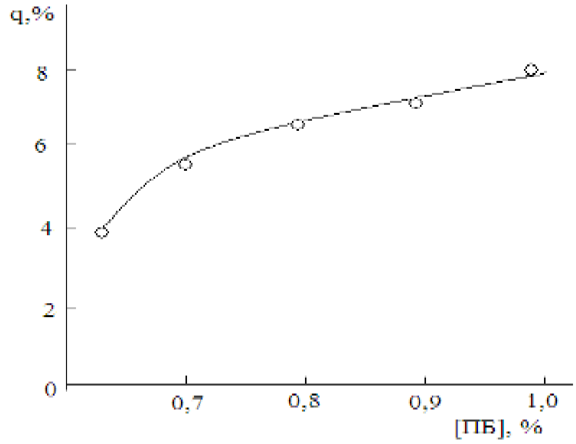

Fig.4. Dependence of the polymerization rate on the concentration of the initiator PB. [AH]=0.5 mol/l, concentration H_2SO_4 = 75 %, 60°C.

The investigated process contains a relatively small amount of polymer. To clarify the possibility of increasing its content in the product, the effect of the initial concentration of AN on the kinetics of synthesis and properties of polyacrylamide was investigated. As the concentration of the initial monomer increases, the reaction rate and polymer yield increase (Fig.5).

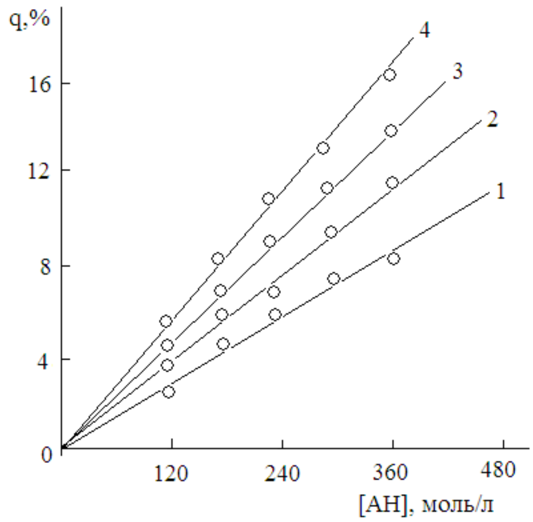

Fig.5. Dependence of the polymerization reaction rate on the concentration of AN, mol/l: 1-0,5; 2-1,0; 3-1,25; 4-1,5. H_2SO_4=75 %, PB= 1,0%, 60° C.

However, at the same time, solubility in water becomes increasingly difficult (even with an increase in the initiator concentration), which prevents a further increase in the polymer content.

An increase in temperature from 60 to 80 ° C led to an increase in the reaction rate, a decrease in its duration and the viscosity of the resulting polymer.

Studies have shown that changes in factors such as temperature and monomer content affect the rate of hydrolysis and polymerization reactions approximately equally and do not lead to a significant change in the composition of the polymer formed during single-stage synthesis. On the contrary, the concentration of the acid or initiator mainly affects one of the reactions, which, along with a change in viscosity, affects the composition of polymer macromolecules. Optimal synthesis conditions were found: [AH]=1.0 mol/l; [H2SO4] =80%; [PB] =1.0%; temperature 60 ^{o}C.

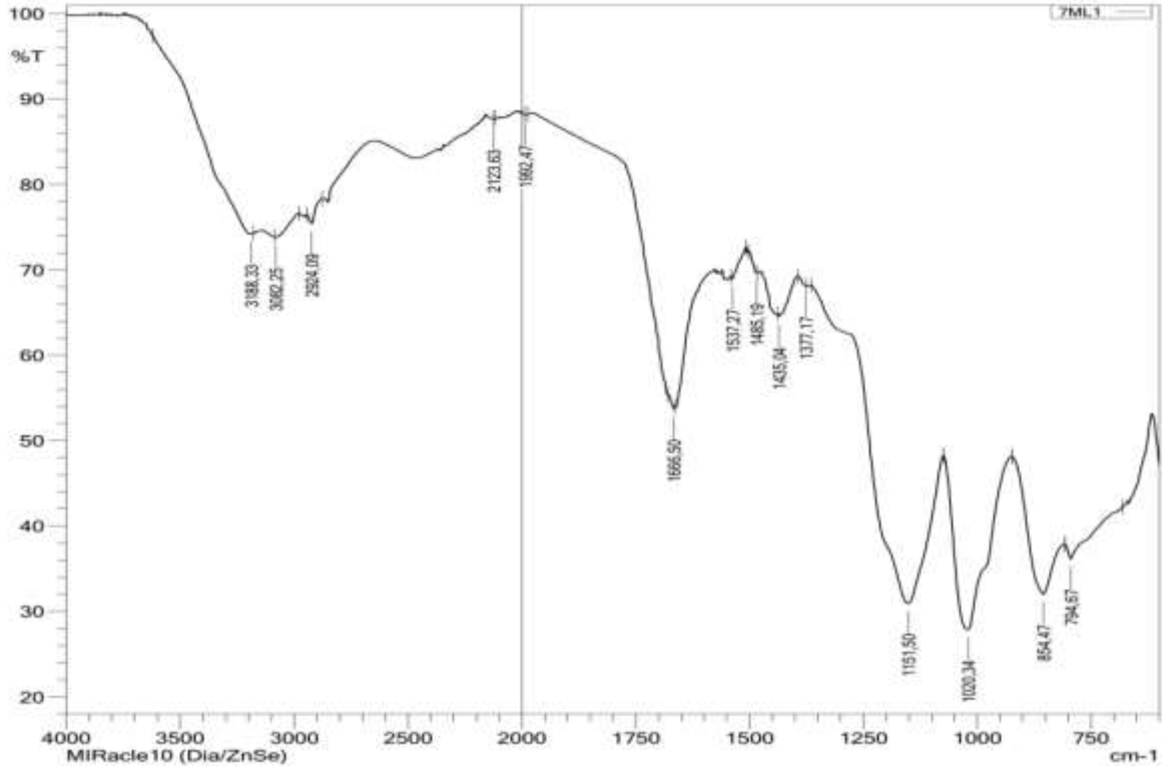

Fig.6. IR Spectroscopy of polyacrylamide

The hydrolysis reaction of acrylonitrile with sulfuric acid and polymerization of the resulting acrylamide in the presence of benzoyl peroxide was carried out by a single-stage method. The influence of the concentration of sulfuric acid, initiator, acrylonitrile was studied and the optimal condition of the process was found.

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