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# INVESTIGATION OF ANIONIC POLYMERIZATION OF ACRYLAMIDE MONOMERS

Shamadinova Nargiz Erkinovna
Senior Lecturer, Tashkent Institute of Chemical Technology
E-mail: nargisxon@mail.ru

Salixova Ozoda Abdullayeva
Candidate of Technical Sciences, Associate Professor of the Tashkent
Institute of Chemical Technology
E-mail: ozodaxon.salihova@gmail.com

## Annotation

It was found that M,M-diethanolacrylamide and M,M-diethanol(met)acrylamide does not react with anionic polymerization; the reasons for this behavior of these monomers have been identified. It is shown that the products of anionic polymerization of acrimides are hyperbranched copolymers containing fragments of heterocain and carbocain structures. Macromolecules have amide and acrylamide groups as end groups; terminal tert-butoxide groups from the polymerization initiator used have been found in some macromolecules. The glass transition and melting temperatures of the anionic polymerization products of the studied acrylamide monomers were measured.

**Keywords:** anionic polymerization, n-methylolacrylamide, tert-butanol, acrylamide, diethanolamine, acryloyl chloride, methacrylyl chloride, carbon-chain polymers, monomers, adsorption chromatography.

## Introduction:

Even in the earliest works on the anionic polymerization of acrylamide monomers containing groups with a labile hydrogen atom, it was found that due to the proton transfer reaction to the growing active center, heterocain polymers are formed instead of the expected carbon-chain polymers, the production of which by other methods is either impossible or extremely difficult [1-3]. Recently, there has been a noticeable increase in interest in the anionic polymerization of acrylate monomers containing groups with a mobile hydrogen atom [4-6].

Studies of the mechanism of anionic polymerization of hydroxyalkyl-(met)acrylates [2-4] have shown that the actual mechanism of polymerization of these monomers is very complex. The paper presents the results of the study of anionic polymerization of a number of acrylamide monomers, such as diethanol-acrylamide (DEAA), diethanol-methacrylamide (DEMAA) and N-methylolacrylamide (MAA), synthesized according to our improved methods [4,5]. The thermodynamics, kinetics and mechanism of anionic polymerization and the structure of the resulting polymers were studied in the most detail using the examples of N-isopropylacrylamide (IPAA), acrylamide and MAA as typical representatives of the class of acrylamide monomers with a mobile hydrogen atom H.

## The Experimental Part

tert-Butanol was purified by distillation in argon current at 82 °C. THF was drained by boiling over KOH, then over metallic potassium, followed by distillation in argon current at atmospheric pressure. DMFA was distilled over barium oxide or calcium hydride in vacuum. Pyridine was boiled over No. OH, then aged and distilled over SaN2 in argon current at atmospheric pressure. The inhibitor 2,2,5,5-tetramethylpiperidine-K-oxide was used without additional purification.

By the method of adsorption chromatography, it was found that up to 25% of an impurity containing no double C = C bonds is present in the commercial IPAA monomer. IPAA was recrystallized from hexane. After cleaning, the product contained 97% of the basic substance (according to chemical analysis).

Acrylamide was purified by recrystallization from chloroform.

DEAA and DEMAA were synthesized by N-acylation of diethanolamine with acryloyl chloride and methacryloyl chloride, respectively, in the presence of triethylamine. The synthesis and purification of DEA and DAMA are described in detail in the works.

The synthesis of the MAA monomer was carried out by the well-known reaction of acrylamide with formaldehyde. A detailed method for the synthesis and purification of MAA is given in the work. Formaldehyde was used as a medical 37% formalin. Due to the instability of dehydrated MAA caused by the formation of k, bis(met)acrylamide polymerizing with the formation of a mesh polymer, long-term storage of dry MAA at room temperature leads to a partial loss of solubility in water and THF. In this regard, MAA was stored in a wet state (water content 2-5 wt. %) at -10 ° C and purified immediately before polymerization.

The purity of monomers was analyzed by adsorption chromatography on a liquid chromatograph equipped with two detectors - refractometric (RF chromatograms) and ultraviolet (UV chromatograms), on a reprosil 100 phenyl column. As eluents, a mixture of methanol-water in a ratio of 30: 70 was used for IPAA, DEAA and DEMAA, as well as water (bidistillate) for acrylamide, MEAA and MAA at an elution rate of 0.7 ml/min and a column temperature of 35 ° C. The purity of all monomers obtained after purification was in the range of 95-99%.

The initiator of anionic polymerization was lithium tert-butoxide (tert-BuOLi), synthesized by the method of dissolving a lithium wire suspension in about four times the excess of distilled tert-butanol in a reflux flask in a dry argon current with a gradual increase in temperature from 35 ° C to boiling and to complete dissolution of lithium. The resulting tert-BuOLi solution (~24.6 wt. %) in tert-butanol was filtered at 60 ° C in argon current, followed by vacuuming at room temperature for 5 hours at ~ 0.05 mmHg (75% yield). The purity of tert-BuOLi was tested by direct titration of 0.1 N with an aqueous HCl solution. The product of 95% purity was stored in argon at room temperature in a desiccator with a drying agent and analyzed before each series of experiments.

Anionic polymerization of the studied monomers was carried out in freshly dried solvents (THF, DMFA or pyridine) in an inert atmosphere in the range of 30-80 ° C, varying the ratio of concentrations of monomers and initiator from 6 to 75 (Table 1). To prevent thermally induced radical polymerization, the processes were carried out in the presence of additives of the nitroxyl radical 2,2,6,6-tetramethyl-1-piperidyloxyl in an amount of ~0.04 wt. %.

Anionic polymerization of IPAA was carried out in THF or DMFA, while the reaction proceeded under homogeneous conditions throughout the process.

With an excess of CHCl3, the growing active centers were neutralized by adding two to three drops of dilute HCl to a neutral reaction, followed by two to three times washing with water from the formed lithium salts. The organic layer was separated from the water layer, dried from moisture residues over molecular sieves 4A and the solvent was distilled. The yield of the IPAA oligomer is 69%.

The product of anionic polymerization of MAA in THF precipitated during the reaction, which was separated by solvent decantation, and to neutralize the growing active centers was mixed with acidified HCl water to a neutral reaction, filtered and washed on a filter sequentially with ice water and ethyl ether, followed by drying from solvents in

Results: In the process of anionic polymerization of unsubstituted acrylamide, a precipitate is formed in pyridine. After decanting the pyridine solution, the precipitate was mixed with water and a few drops of acetic acid were added until a neutral reaction. At the same time, the precipitate was not completely dissolved in water. The aqueous solution of the product was decanted from the sediment, evaporated at 50 ° C and dried in vacuum. The dried residue contained the polymerization product of acrylamide with an admixture of lithium salt. The residue that remained undissolved when mixed with water was washed with water and dried in vacuum. Thus, the polymerization product of acrylamide in pyridine consists of two fractions approximately equal in weight: soluble and non-soluble in water. The product remaining dissolved in pyridine after synthesis and amounting to about 8% by weight of the sum of all the.

Table 1. Effective rate constants at 60 °C, activation energies of anionic polymerization of acrylamide monomers, and glass transition and melting temperatures of the resulting polymers.

| Monomer | *kp^* x $10^4$, л/моль с | *E*$^{эф}$ , кДж/моль | ○ ○ | *T* °ё |
|---|---|---|---|---|
| IPAA | 4.4 | 72.7 ± 7.1 | 58 | 167 |
| Acrylamide | 12.6 | 43.9 ± 2.1 | - | 143/129* |
| MAA | 122 | 35.1 ± 5.8 | 33 | 86 |

In the numerator - the melting point of the polymer fraction soluble in water, in the denominator - insoluble.

Molecular weight characteristics: The experimental values of the degree of polymerization of Pn, the expression of anionic polymerization products obtained by exclusive chromatography, increase linearly with the conversion of a (Fig.1) and are described by the expression.

P, EXP

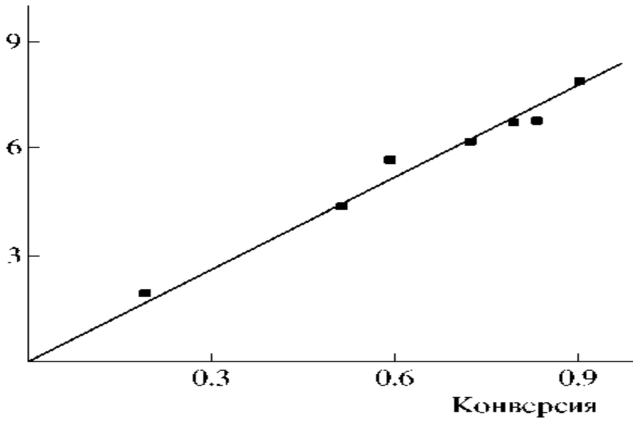

Fig. 1. Dependence of the experimental degree of polymerization of the IPAA anionic polymerization product on conversion.

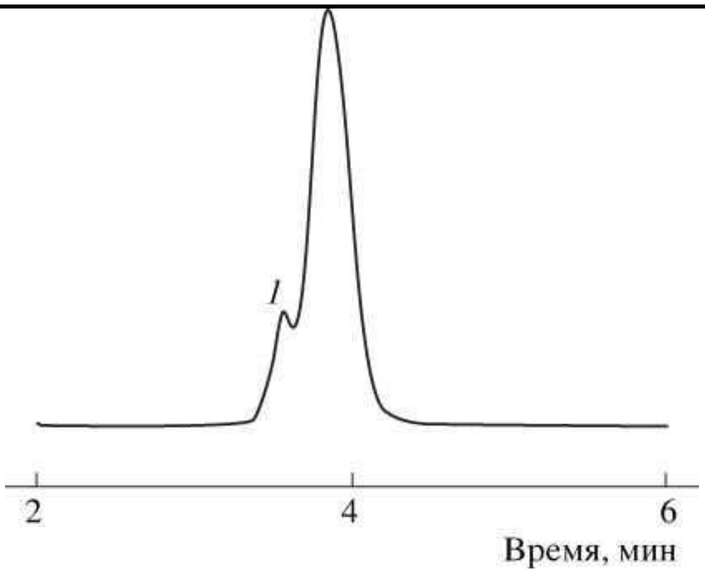

Fig. 2. Chromatogram under critical conditions of the IPAA anionic polymerization product.

The limiting experimental values of Pn, ^ of the studied acrylamide monomers (Table.1) are close to the maximum calculated values of Pn, that is, equal to the ratios of the initial concentrations [M]0 : 0. These experimental facts clearly indicate that the growing polymer chains in the systems under study develop according to the kinetic law characteristic of “living” chains, and the polymerization system itself in the absence of breakage agents and transmission circuits are “live". It should be noted, however, that with a decrease in the molar fraction of the initiator in the polymerizing IPAA-mpem-BuOLi system, there is a certain tendency to decrease Mn, which indicates the following: there are impurities in the system that we have not identified, the role of which increases with a decrease in the concentration of growing chains.

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