

Copolymerization of acrylonitrile with a nitrogen-containing ester

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Abstract. In the paper the results of synthesis of binary copolymers with different contents of monomer units by radical copolymerization of 1-chloro-3-piperidino-2-propylacrylate with acrylonitrile in organic solvent medium at 30-60°C in the presence of radical initiator using free-radical polymerization technique not up to high degrees of transformation by gravimetric method are given. Dinitrilazobisobutyric acid was used as the radical initiator. Water and dimethylformamide were used as solvent. Under these conditions in water the process proceeds heterogeneously, and in dimethylformamide homogeneously and with high speed. The synthesis rate of copolymers of 1-chloro-3-piperidino-2-propylacrylate with acrylonitrile in the studied solvents increases with increasing temperature. Experimental studies have shown that copolymerization does not proceed in the absence of the initiator and this indicates a radical nature of the reaction. The structure of synthesized compounds was confirmed by IR, NMR spectral analyses. The participation of multiple bonds of both monomers during copolymerization was determined. The composition of copolymers has been determined which indicates that the copolymer formed at early stages is enriched with 1-chloro-3-piperidino-2-propylacrylate units. The values of relative activities of monomers were calculated by Finemann-Ross method. The found values of copolymerization constants $7:1=0.28$, $7:2=0.62$ and the value of product of copolymerization constants less than unity that both types of formed polymer radicals react much faster with foreign monomer than with their own.

1. Introduction

Acrylonitrile stands out as a significant monomer among the various nitriles employed in industrial applications. Its derivatives and the materials originating from it showcase a diverse array of valuable and distinctive characteristics. These compounds hold substantial potential within organic synthesis and offer an array of practical applications. They find utility as agents combating microbial growth, flocculants featuring rare earth elements, substances countering corrosion, as well as polymers capable of forming fibers and serving as copolymers with specialized attributes. Given this context, the exploration and enhancement of the assortment of fiber-forming polymers built upon acrylonitrile, along with the meticulous investigation of their qualities, hold both theoretical and practical significance.

When obtaining fiber-forming polymers based on acrylonitrile, the main method of synthesis is radical copolymerization in solution, as this method has a number of advantages and disadvantages. The advantages of the method include further use of spinning solutions in the formation of fiber, as well as at copolymerization in organic solvents used equipment is much less exposed to corrosion [1].

In modern organic synthesis there is a steadily growing interest in the use of safer organic solvents. Much attention among them, pay great attention to ionic liquids, characterized by incombustibility and the possibility of repeated use in the recycling [2]. The authors studied the regularities of radical polymerization and copolymerization with methyl methacrylate in ionic liquids based on 1,3-dialkyl-substituted imidazole [3]. It has been shown that polymerization and copolymerization reactions in medium of liquid organic salts lead to the formation of (co)polymers in high yield and high molecular weight.

Copolymers consisting of acrylonitrile and acrylic acid were synthesized by alternative researchers using a DMSO medium [4]. Their findings indicated that as the proportion of acrylic acid within the copolymer was augmented, there was a noticeable rise in the influence of the ionic cyclization mechanism. This phenomenon contributed to the widening of the temperature range conducive to cyclization and concurrently led to a reduction in the intensity of heat flux. The authors'

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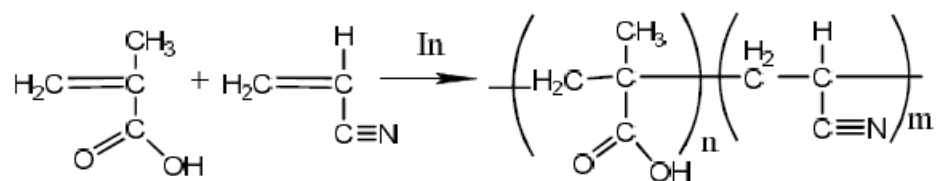
studies allowed to propose a new way to control the properties of AH - AK copolymer during its heat treatment, namely combination of RAFT mechanism with dosed introduction of co-monomer in polymerization. In this work, the graft radical copolymerization of polyacrylonitrile (PAN) and lignin was investigated [5]. By studying the ratio of reacting components on the course of reaction it was shown that the addition of acrylonitrile to lignin molecules leads to an increase in the molecular weight of the copolymers. Within this investigation, a copolymer of poly(acrylonitrile-co-methyl methacrylate) was employed. This copolymer was synthesized through a radical polymerization process involving acrylonitrile (AN) and methyl methacrylate (MMA) as co-monomers [6]. The polymerization procedure was executed utilizing potassium persulfate as the initiator, maintaining a 1:1 ratio of acrylonitrile and methyl methacrylate monomers. New environmentally friendly methods for the synthesis of acrylonitrile copolymers in ionic liquids and supercritical media have been analyzed [7]. The methods of synthesis of acrylonitrile copolymers which can be used for spinning fibers from the melt have been considered. A patent search has been performed, the information relating to new methods and recipes for the synthesis of acrylonitrile copolymers has been summarized. In this article, the synthesis and assessment of hybrid benzimidazole-acrylonitrile derivatives are detailed, focusing on their antimycobacterial efficacy against *Mycobacterium tuberculosis* H37Rv in vitro [8]. Within the range of derivatives explored, compound 3b demonstrated the highest level of activity, displaying a minimum inhibitory concentration (MIC) of 0.78 mg/ml against *M. tuberculosis*.

The researchers in this study explored a range of model nanoparticles, specifically rigid poly[acrylonitrile-co-(N-vinylpyrrolidone)], that were loaded with Nile Red or Rhodamin B [9]. The surface characteristics of these nanoparticles were modified by adjusting the molar content of hydrophilic NVP, varying from 0 to 24.1%, while the particle size spanned from 35 to 244 nm. Additionally, itaconic acid monoesters and monoamides, including 2-carbamoylmethacrylic acid, N-octyl-2-carbamoylmethacrylic acid, and 2-methoxycarbonylmethacrylic acid, were effectively employed in the thermal cyclization process of acrylonitrile copolymers [10]. Through a copolymerization reaction, aminated polyacrylonitrile-transplant-chitosan (APANCS) copolymers were synthesized using diethylene triamine and polyacrylonitrile-transplant-chitosan (PANg-CS) as precursors [11]. Specifically, PAN-g-CS copolymers were prepared through graft polymerization, utilizing acrylonitrile, chitosan, and a free radical initiation process with cerium ammonium nitrate (CAN) as the initiator, in the presence of air.

The study further delved into the ternary copolymerization of acrylonitrile, methyl acrylate, and isoconic acid in a dimethyl sulfoxide solution within a temperature range of 20 to 80°C, catalyzed by symmetrical trithiocarbonates [12, 13]. The impact of synthesis conditions, encompassing temperature and the presence of a chain transfer agent, on the kinetics of the cyclization reaction was thoroughly examined.

In regard to copolymers of acrylonitrile and acrylic acid, the authors conducted synthesis in DMSO with a 40% content of co-monomers in the reaction mixture [14]. Various methods of introducing acrylic acid into the reaction were experimented with, leading to the observation that an increase in the proportion of acrylic acid within the copolymer resulted in a heightened contribution of the ionic cyclization mechanism. This, in turn, positively influenced the expansion of the temperature range favorable for cyclization while concurrently reducing the intensity of heat flux.

Moreover, acrylonitrile and methacrylic acid copolymers were successfully synthesized through copolymerization in an aqueous solution [15]. The general form of the co-polymerization reaction between AN and MAC can be described as follows:



The researchers extensively investigated how the conditions of copolymerization influenced both the molecular weight and composition of the resultant copolymers. Notably, they determined that performing copolymerization within an aqueous dextran solution effectively prevented the agglomeration of the formed copolymer particles, leading to minimal alterations in its composition.

In a separate study, the synthesis of copolymers comprising acrylonitrile, methyl acrylate, and 2-acrylamide-2-methylpropanesulfonic acid was carried out within a dimethylformamide medium at a temperature of 70°C [16]. The findings indicated that an increase in the water content within the reaction medium, ranging from 0.3% to 3.6% by weight, did not adversely impact the synthesis kinetics of these copolymers. Furthermore, this adjustment had no detrimental effects on the physical and mechanical properties of the fibers obtained from these copolymers. It has been shown that in order to reduce the solvent regeneration costs the water content in the regenerated DMF can be increased from 0.05 to 1.00% (wt.). In other paper the synthesis of acrylonitrile copolymers with Itaconic acid derivatives in solvent medium with

addition of radical polymerization initiator at temperature 65-85°C and supercritical carbon dioxide was used as a solvent [17]. Itaconic acid derivatives are its monoesters or monoamides, and the content of itaconic acid derivatives in the copolymer ranges from 0.01 to 4 mole % [18]. The authors have performed radiation copolymerization of acrylonitrile with co-monomers selected from acrylic and methacrylic acid based ester groups, with the proportion of co-monomers not exceeding 20% in the copolymer. The reaction is carried out in aqueous dispersion medium containing cationic or anionic emulsifier at an emulsion monomer to water phase ratio from 5 to 95 to 20 to 80, at temperatures from 5 to 60°C, at an irradiation dose rate from 0.02 to 0.2 Gy/s to monomer conversion degree from 80 to 95% to obtain latex with a diameter of latex particles from 80 to 110 nm.

In this work the authors performed pseudo vivo radical binary copolymerization of acrylonitrile with methyl acrylate, strol and tert-butyl acrylate in mass in the presence of reversible chain transfer agent dibenzyl tritiocarbonate [19]. Conditions for obtaining acrylonitrile copolymers with narrow molecular weight distribution are shown.

The aim of this work is to synthesize binary copolymers based on acrylonitrile with unsaturated nitrogen-containing ester and to study their structure and properties. 1-Chloro-3-piperidine-2-propylacrylate was chosen as a nitrogen-containing ester.

2. Materials and methods

Acrylonitrile (AN) was subjected to purification from inhibitors through a multi-step process. Initially, it was treated with a 5% alkali solution to remove inhibitors. Subsequently, it underwent a thorough washing with distilled water until it reached a neutral reaction. Afterward, it was dried using calcium chloride as a desiccant. Finally, the purified acrylonitrile was distilled under atmospheric pressure, yielding a boiling point of $T_{\text{kip}}=77^{\circ}\text{C}$. The resulting purified acrylonitrile had a refractive index of $n_{20\text{D}}=1.3914$.

The synthesis of 1-Chloro-3-piperidine-2-propylacrylate was carried out and subsequently purified using an established method. The characterization of the compound was conducted through IR spectroscopy, following the procedure outlined in previous work [20]. The IR spectrum of 1-chloro-3-piperidin-2-propanol contains the following absorption bands, cm^{-1} : $\nu(\text{C-N})$ 3359; $\nu(\text{CH}_3)$ and $(-\text{CH}_2)$ 2248; $\nu(\text{C=O})$ 1651; $\nu(\text{C=C})$ 1635; $\nu(\text{C-O-C})$ 1293. $\text{C}_{11}\text{H}_{18}\text{NO}_2\text{Cl}$; $d_{20}^{20}=1.2030\text{g/cm}^3$, $n_{20}^{20}=1.3660$. The organic solvents were purified according to known methods [21].

The physico-chemical characteristics of the compounds aligned with the values reported in existing literature. For the experiments, Ammonium persulfate (PA) of "Ch" grade with a purity of 99% was utilized without any further purification steps. Ammonium persulfate, chemically represented as $(\text{NH}_4)_2\text{S}_2\text{O}_8$, is composed of monoclinic crystals and exhibits good solubility in water, possessing a density of 1.982 g/cm^3 . Its decomposition occurs at a temperature of 120°C.

The copolymerization reaction was carried out in glass shaped tubes. Necessary amount of initiator was placed in clean tubes with ground plugs and solvent, acrylonitrile, 1-chloro-3-piperidino-2-propylacrylate were poured in the required ratios. The mixtures were stirred until the initiator dissolved, then the tubes were purged with inert gas, carefully closed with glass stoppers and placed in thermostat at the set temperature. The copolymerization reaction was carried out to conversion rate of 7.4%. At its completion the reaction mixture was cooled to room temperature and opened. The copolymers were redeposited from dimethylformamide solution with ethyl acetate. The copolymers were redeposited twice, the copolymer precipitate was separated and dried in vacuo until constant weight. The obtained copolymers are white powdery products, which are soluble in dimethylformamide, dimethylsulphoxide, acetone, dioxane. The conversion of the copolymers was determined by gravimetric method. The copolymerization reaction was carried out in Wited thermostat at temperatures $20-60\pm 0.1^{\circ}\text{C}$.

IR spectra of the initial reagents and synthesized copolymers were taken on FTIR spectrophotometer SISTEM-200 in the range of wave numbers $400-4000\text{ cm}^{-1}$ in KBr tablets. PMR spectra of the substances solutions in CD_3COCD_3 were recorded on spectrometer "Variant-6" with operating frequency at 60.0 MHz H nuclei at 30°C. A small amount (~1%) of TMC was also introduced into the ampoule as an internal reference. Thermogravimetric and differential thermal analysis were recorded on a DTG- 60 series instrument (Shimadzu, Japan). The device has high-precision scales, sensitive detectors and uniform temperature distribution in the furnace provide the ability to register the change in sample mass up to 1000 mg with an accuracy of 0.1 μg in a wide range of DTA measurements: from $\pm 1000\text{ }\mu\text{V}$.

3. Results and discussion

Binary copolymerization of 1-chloro-3-piperidin-2-propylacrylate (CPPAC) with acrylonitrile (AN) was carried out in organic solvent medium at temperatures 30-60°C in the presence of radical initiators. Water and dimethylformamide served as solvent. Under these conditions in water the process proceeds heterogeneously, and in dimethylformamide homogeneously and with high speed.

The copolymerization of CPPAC with AH was studied by gravimetric method. At the same time in one series of experiments reaction was carried out with low degrees of conversion - to calculate copolymerization constants r_1 and r_2 , in the other - to deep degree of conversion in order to study the properties of the synthesized copolymers. In order to

determine the effect of initial monomer ratio on the composition of the resulting copolymers the copolymerization of CPPAC with AH was carried out in a wide range of monomer ratios (Table 1).

Table 1. Dependence of the composition of copolymers of CPPAC (M_1) with AH (M_2) on the ratio of monomers in the initial mixture in DMF medium: $[pa]=5 \cdot 10^{-3} \text{mol/L}$; $t=40^\circ\text{C}$.

Initial ratio, mole fraction		Chlorine content, %	Output, %	Composition of copolymer, mole fraction	
M_1	M_2			m_1	m_2
0.20	0.80	3.35	2.3	0.24	0.76
0.35	0.65	5.40	3.5	0.36	0.64
0.50	0.50	6.36	4.9	0.42	0.58
0.65	0.35	8.20	6.0	0.54	0.46
0.80	0.20	9.60	7.4	0.63	0.37

As can be seen from Table 1, the ratio of monomer units in copolymers does not correspond to their ratio in the initial mixture. This ratio shift is determined due to the difference in activity of the co-monomers. If the ratio of CpAc to NA is 0.20:0.80 then it gives the copolymer which is enriched with CpAc units. It is soluble in water, however, as the relative fraction of AH in solution increases, the fraction of AH units in the resulting macromolecules increases and the copolymer is no longer soluble in water.

Based on the dependence of copolymer composition on the ratio of monomers in the initial mixture were determined copolymerization constants for AH-CPPAC system by the method [22, 23]. They were determined on the basis of experimental data on copolymerization of these systems by graphical solution of Feinman-Ross differential equation (Table 2).

The information presented in Table 2 demonstrates that both constants, r_1 and r_2 , exhibit values below one. This observation suggests that the actively growing radicals have a higher tendency to engage with monomers from outside their own group rather than those from their own group. Furthermore, the product of copolymerization constants, denoted as $r_1 \cdot r_2$ and equal to 0.17, is also below unity. This signifies a pronounced inclination of the monomers to alternate in the copolymerization process.

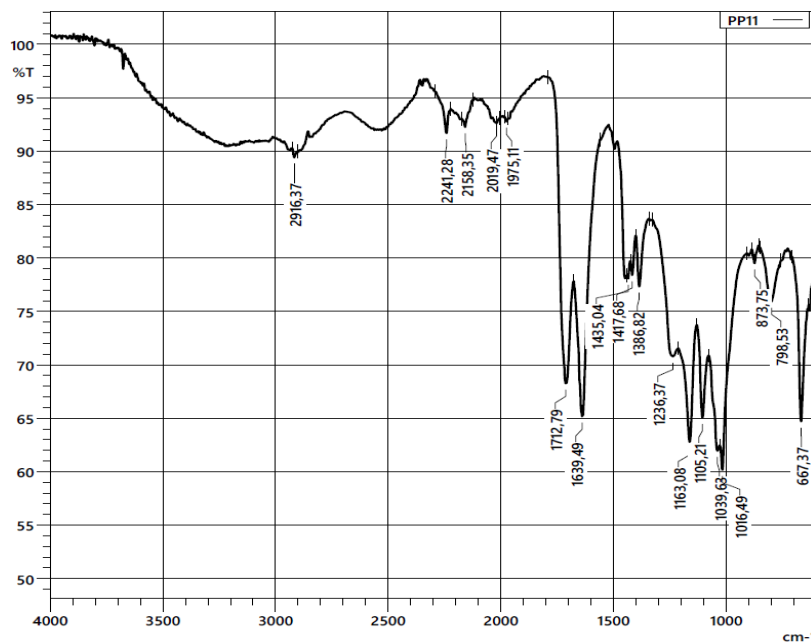


Fig. 1. IR spectrum of copolymer based on CPPAC with AH at a ratio of 0.35:0.65.

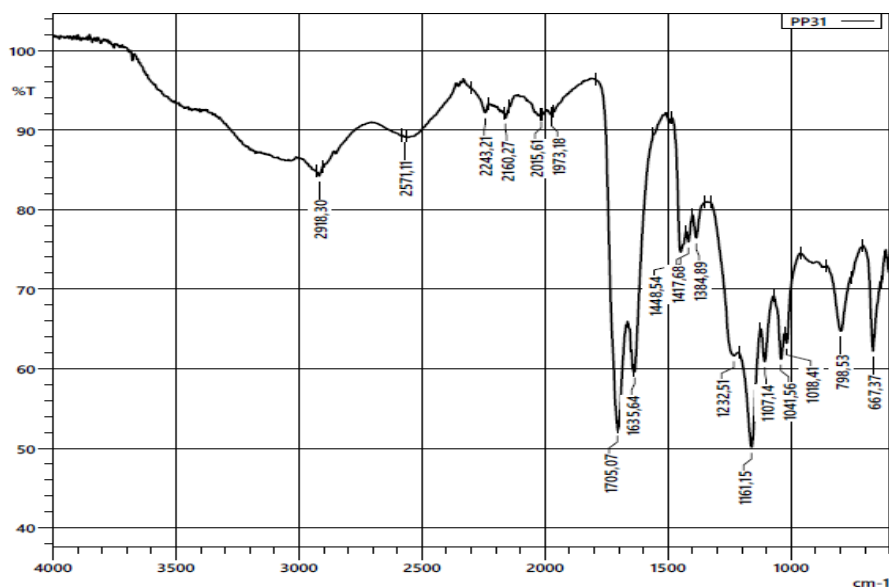


Fig. 2. IR spectrum of copolymer based on CPPAC with NA at a ratio of 0.65:0.35.

The chemical composition and structural integrity of the produced copolymers were verified through elemental analysis, infrared (IR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. IR spectra of copolymers based on CPPAC and AK at 0.35:0.65 and 0.65:0.35 ratios obtained at small degrees of transformation are shown in Figures 1 and 2.

Table 2. Values of effective copolymerization constants in AH-HPPAC system.

Systems	r_1	r_2	$1/r_1$	$1/r_2$	$r_1 r_2$
AH-HPPAC	0.28	0.62	3.57	1.61	0.17

The IR spectroscopy data confirm the production of a new copolymer of CPPAC with AH. In the spectra of the copolymer samples one can observe the absorption bands characteristic of both CPPAC fragments in the region of 1705- 1712 and 1016-1236 cm^{-1} (ester), at 1635-1639 cm^{-1} the valent vibrations of carbonyl group C=O, and the absorption bands of nitrile C≡N groups in the region of 2241-2243 cm^{-1} and strain symmetric vibrations of CH_2 at 1435 and 1448 cm^{-1} , respectively. The absence of absorption bands characteristic of double C=C bonds in the IR spectra of copolymers indicates that the copolymerization reaction proceeds in the vinyl groups of the initial monomers.

Nuclear magnetic resonance (NMR) spectroscopy was employed to analyze the structure of copolymers generated at various ratios of co-monomers, focusing on carbon-13 (C-13) nuclei (as depicted in Figure 3).

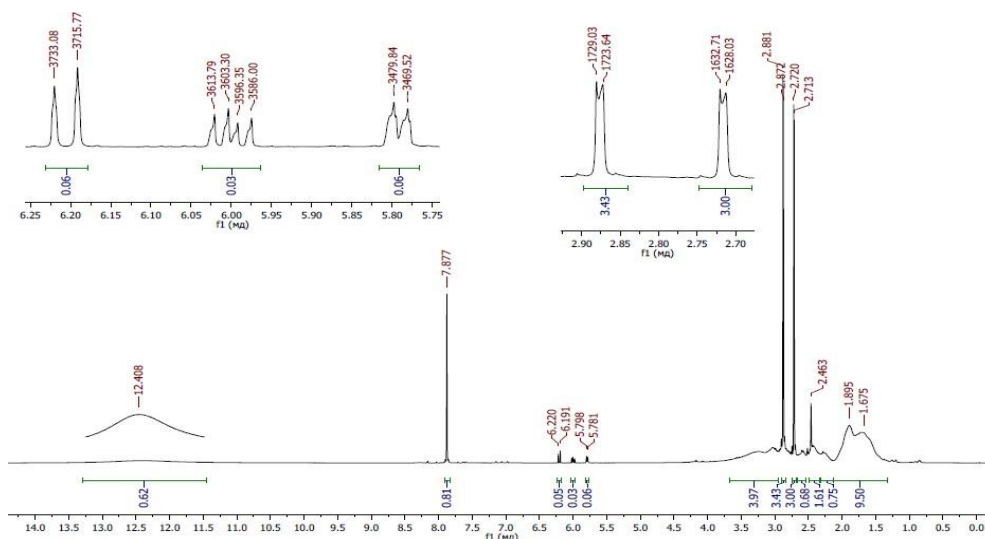


Fig. 3. ¹H NMR spectrum of CPPAC copolymer with AH at 1:1 ratio.

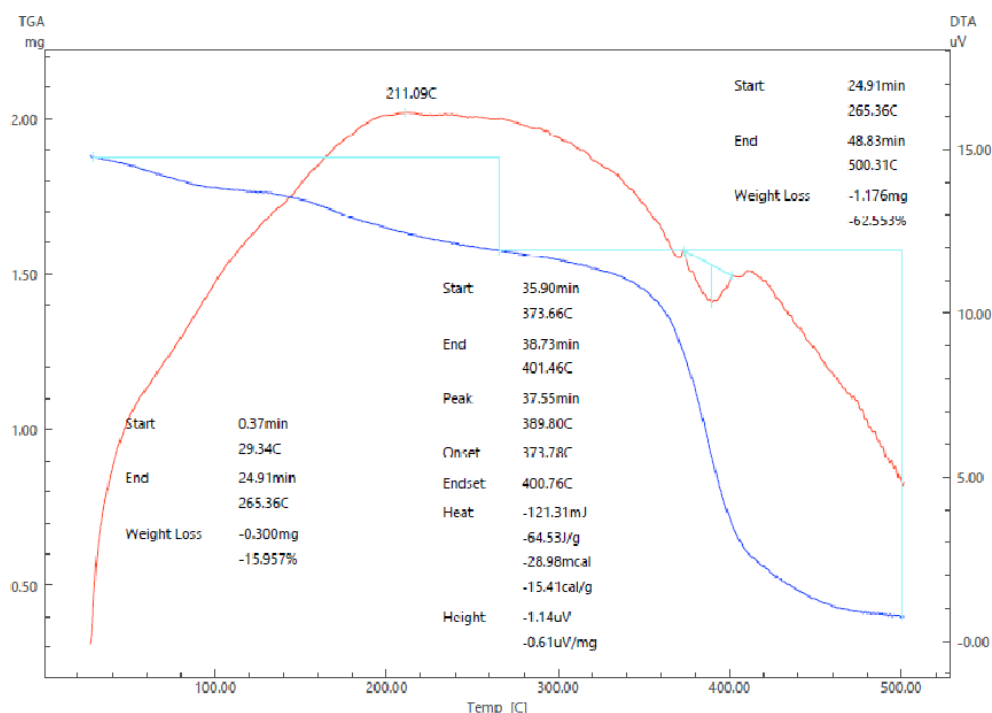


Fig. 4. Thermogram of CPPAC copolymer with AH at 0.35:0.65 mole fraction ratio at 40°C.

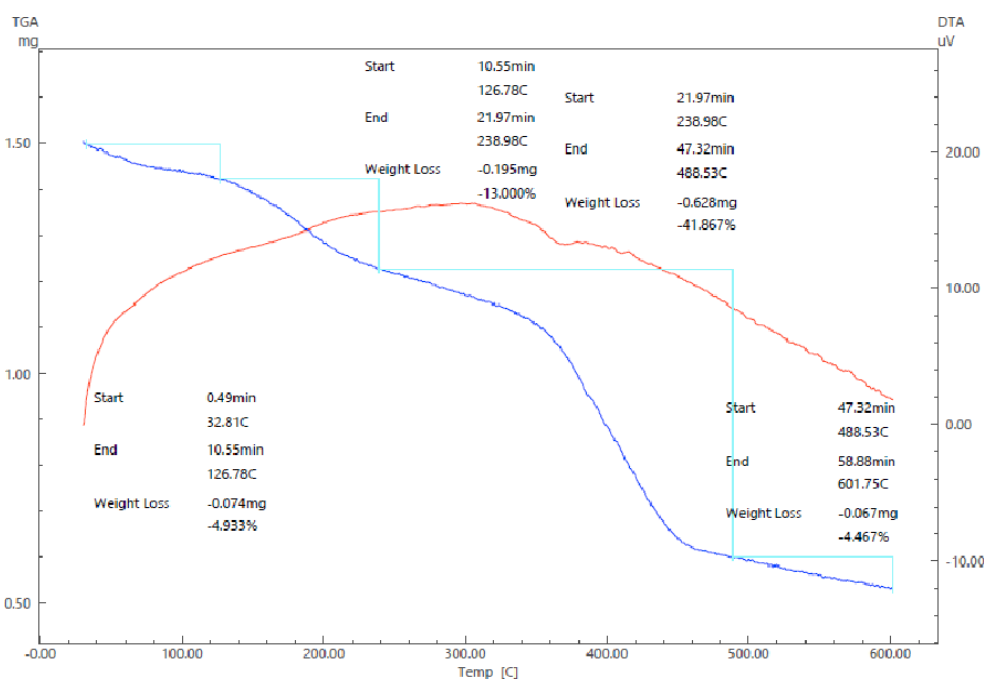
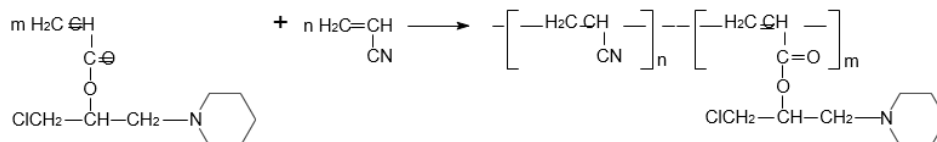


Fig. 5. Thermogram of CPPAC copolymer with AH at a ratio of 0.65:0.35.

In the proton nuclear magnetic resonance (^1H NMR) spectrum of the copolymer derived from AH and CPPAC (as illustrated in Figure 3), distinct signals manifest within the range of 1.6-1.8 ppm, which correspond to the protons of methylene groups. Additionally, signals at 7.8 ppm correspond to carbon atoms with a single attached proton (CH group), while a broadened signal at 12.4 ppm corresponds to protons of CN, CH, and CH₂ groups from acrylonitrile. Hence, taking into account the elemental analysis, infrared spectroscopy (IR), and ^1H NMR spectra, the structure of the copolymer based on AH and CPPAC can be delineated as follows:



Thermogravimetric analysis was carried out to evaluate the thermal stability and thermal degradation of CPPAC copolymers with AH (Figures 4 and 5). As can be seen from Figure 4, the DTA curve of AH-based copolymer with CPPAC is characterized by an endothermic maximum at 211°C and the presence of one glass transition region (273 °C), which confirms the thermodynamic compatibility of the components.

The transition of the copolymer from glassy to elastic state is observed at 373°C. Obtained kinetic curves TGA thermal degradation show that the copolymers when heated to 265°C lose only 4.47% of weight.

4. Conclusions

1. The radical copolymerization of 1-chloro-3-piperidin-2-propylacrylate with acrylonitrile in dimethylformamide medium at different initial monomer ratios by radical copolymerization in the presence of ammonium persulfate as radical initiator at 40°C was studied.
2. The composition of synthesized copolymers has been determined by elemental analysis. It has been shown that ratio of monomer units in copolymers does not correspond to their ratio in initial mixture. This ratio shift is determined due to the difference in activity of co-monomers.
3. The relative activities of 1-chloro-3-piperidino-2-propylacrylate and acrylonitrile were determined by Feinemann-Ross method. The found values of copolymerization constants are $n_1 = 0.28$ and $n_2 = 0.62$, respectively.

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