

Controlled Copolymerization of Acrylonitrile and Ethyl 2-cyanoacrylate under Reversible Addition-Fragmentation Chain Transfer Conditions and Thermal Behavior of the Obtained Copolymers

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Abstract—Copolymers of acrylonitrile and ethyl 2-cyanoacrylate have been synthesized for the first time. It has been shown that the copolymers with controllable molecular mass and narrow molecular mass distribution are formed under conditions of radical initiation in the presence of 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid as a reversible chain transfer agent. Relative reactivities of the monomers in the copolymerization ($r_1 = 0.052 \pm 0.02$ for acrylonitrile and $r_2 = 54.5 \pm 7.2$ for ethyl 2-cyanoacrylate) have been determined. Copolymers with different microstructure have been synthesized using different methods to introduce ethyl 2-cyanoacrylate in the copolymerization (simultaneous and continuous charging). It has been shown that two competing processes, depolymerization and cyclization of the nitrile units, occur during heating of the copolymers under inert atmosphere. Probability of depolymerization has been increased with the increase in the fraction of ethyl 2-cyanoacrylate in the copolymer and the change of the gradient copolymer structure to the statistical one.

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INTRODUCTION

Acrylonitrile copolymers have been conventionally used in the production of textile and carbon fiber [1–3]. Such copolymers usually contain various vinyl monomers, including (meth)acrylates, vinyl acetate, vinyl acids, etc. [4–17]. Nevertheless, the search for new copolymers which can aid in broadening the temperature range of thermooxidative stabilization and shifting it towards lower temperature is still ongoing. In practice, two comonomers are often used to do so: a cyclization accelerator (acrylic, methacrylic, or itaconic acid) and an internal plasticizer (for example, methyl acrylate) [18, 19]. The said properties of two comonomers could not be combined so far.

In this study, we suggested that ethyl 2-cyanoacrylate (ECA) containing both nitrile and ester groups in a single monomer unit could be utilized to resolve the issue. Alkyl 2-cyanoacrylates have been widely used as cyanoacrylate glues [20]. A combination of two acceptor substituents at the same carbon atom facilitates the cyanoacrylates polymerization via the anionic mechanism in the presence of even weak nucleophiles (water, alcohols, and others) [21–

26]. Zwitter-ionic polymerization of cyanoacrylates under the action of DMSO and other reagents has been described as well [21, 27, 28].

Radical polymerization of alkyl cyanoacrylates under the action of conventional initiators, benzoyl peroxide and AIBN, has been reported [29–35]. It can occur if the anionic polymerization is suppressed, which is possible in the presence of a series of strong acids (sulfuric, dichloroacetic, trifluoroacetic, and methanesulfonic acids, 1,3-propanesultones, etc.). Kinetic features of radical polymerization of alkyl cyanoacrylates are analogous to these of other vinyl monomers, for instance MMA. However, alkyl cyanoacrylates are more reactive towards polymerization than methacrylates [36]. For example, the rate constant of chain propagation of ECA at 30°C has been of 1.6×10^3 L/(mol s) [32], corresponding to this of MMA at 80°C [37].

Copolymerization of ethyl cyanoacrylates with monomers bearing electron-donor substituents has afforded alternating copolymers [36, 38, 39]. This trend has been found typical of vinyl ethers, vinyl acetate, styrene, α -methylstyrene, and MMA. AN copo-

lymers with alkyl 2-cyanoacrylates have not been described in scientific and patent literature, except for dicyclohexylammonium salt of cyanoacrylic acid [40, 41]. In the latter case, it has been found that this comonomer favors broadening of the temperature range of cyclization, due to the presence of the carboxylic group in the monomer structure.

Alkyl cyanoacrylates can be polymerized via the reversible addition-fragmentation chain transfer (RAFT) radical polymerization [42], which has been demonstrated by the synthesis of the block copolymer with MMA under the action of cyanoisopropyl dithiobenzoate as the reversible chain transfer agent. However, the authors have found that the dithiobenzoate fragment can be eliminated from the macromolecule in the form of dithiobenzoic acid, which can disrupt the RAFT mechanism and lead to the formation of the terminal C=C bonds. Using ethyl, butyl, and phenylethyl 2-cyanoacrylate as examples, it has been found that the fraction of the "living" chains during the polymerization is of 30%.

At the same time, poly(alkyl cyanoacrylates) have been found unstable at heating or under the action of a series of basic reagents and readily decompose [43–47]. They depolymerization is possible at temperature slightly above the glass transition temperature [48]. Heating of poly(ethyl 2-cyanoacrylate) above 165°C has led to depolymerization, activation energy of the process being 37.4 kcal/mol [49]. The increase in the length of the alkyl substituent has led to increase in the depolymerization activation energy [43, 50].

Heating of the copolymers obtained via copolymerization of AN with alkyl cyanoacrylates can be expected to lead to partial decomposition due to the presence of the alkyl cyanoacrylate units, the formed radicals inducing cyclization of the nitrile groups of AN.

Hence, this study aimed to synthesize novel copolymers of AN and ECA under conditions of RAFT process and to investigate their thermal behavior.

EXPERIMENTAL

The following monomers were used: AN (99%, Acros) purified via distillation using the conventional procedure and ECA (98%, Weisse) used as received. The initiator AIBN was recrystallized from ethanol and stored in dark at -3°C . DMSO (99%) and DMF (HPLC grade) purchased from Fluka was distilled prior to the use. The RAFT agent, 2-(dodecylthiocarbonylthio)-2-methylpropionic acid (DTMPA, 99%), and the inhibitor of anionic polymerization, *p*-toluenesulfonic acid (TSA, 99%), were purchased from Aldrich and used without additional purification.

Copolymerization of AN and ECA (1–40 mol %) to assess the relative reactivity of the monomers were performed in DMSO at 80°C in the presence of 0.2 wt % of TSA with respect to the total volume and

3×10^{-3} mol/L of AIBN. The polymer was isolated at low conversion (up to 10%) via precipitation of the polymerize into an acetone-hexane mixture (60 : 40, w/w). The obtained polymer was filtered off, washed, and dried at 60°C , and the copolymer composition was analyzed.

RAFT copolymerization of AN with ECA was performed similarly. Calculated amounts of AIBN and DTMPA (3×10^{-3} mol/L) as well as TSA (0.2 wt %) were dissolved in DMSO, so that total concentration of the monomers in the solution was 40 wt %. Two methods were used to introduce the monomers in the synthesis. In the first case, AN and ECA were added simultaneously; in the second case, AN was introduced in a single portion, whereas ECA was added at a predefined rate using a syringe pump during the polymerization. A flask with the reaction mixture was purged with argon (99.99%) during 15 min, a reflux condenser was attached, and the flask was immersed in a bath heated to 80°C . The temperature was maintained constant at $\pm 0.1^{\circ}\text{C}$. During polymerization, the reaction mixture was regularly sampled to estimate the conversion and analyze the product. If needed, the sample was diluted with DMSO containing TSA to avoid anionic polymerization of ECA and precipitated in an excess of water containing TSA; the copolymers were filtered off, washed with water, and dried at 80°C to constant mass. The conversion was determined by means of gravimetry.

Molecular mass parameters of PAN were investigated by means of GPC using a GPC-120 chromatograph (PolymerLabs). The analysis was performed at 50°C in DMF containing 0.1 wt % of LiBr, the flow rate being 1 mL/min. Two PLgel $5 \mu\text{m}$ MIXED C columns ($M = (5 \times 10^2) - (1 \times 10^7)$) were used for the separation. Average MM and MMD were calculated using the PMMA references and recalculated to PAN using the coefficients of the Mark-Kuhn-Houwink equation ($K_{\text{PAN}} = 39.4 \times 10^{-4}$, $\alpha = 0.75$, $K_{\text{PMMA}} = 17.7 \times 10^{-4}$, $\alpha = 0.62$ [51]).

Film specimens of the copolymers were analyzed. To do so, 8 wt % of the polymers in DMSO was poured onto a glass support, and the solvent was evaporated at 80°C during 3 h. The films were detached, residual DMSO was extracted with water during 24 h, and the specimens were dried under vacuum at room temperature to constant mass. The prepared films were cut into square pieces (20×20 mm), the film thickness being 50 to 100 μm .

Heat effects observed during dynamic heating of the polymers were investigated using a Netzsch DSC 204 differential scanning calorimeter (Netzsch, Germany) under dry argon atmosphere (flow rate 50 mL/min, temperature range $30 - 500^{\circ}\text{C}$, heating rate 10 deg/min). The measurements were performed with the specimens of 4 to 8 mg using standard aluminum crucible. The results were processed using Netzsch Proteus software.

Thermogravimetric analysis was performed using an STA 449 F3 Jupiter thermal analyzer (Netzsch). The mass loss of the 15–20-mg specimens of the AN copolymers was analyzed during linear heating at 10 deg/min from 25 to 600°C in a corundum crucible under argon atmosphere, the flow rate being 50 mL/min.

Composition of the AN copolymers was determined by means of IR spectroscopy using a Spectrum Two FT-IR Spectrometer instrument (Perkin Elmer), the spectrum range being 4000–400 cm^{-1} . Quantitative composition of the copolymers was determined using the calibration curve of the ratio of absorbance of the bands A_{1730}/A_{2243} on the molar ratio of the ECA and AN units in a mixture of the homopolymers, A_{1730} and A_{2243} corresponding to the intensity of characteristic absorption bands of the C=O stretching ($\nu_{\text{C=O}} = 1730 \text{ cm}^{-1}$) for ECA and the CN stretching ($\nu_{\text{CN}} = 2243 \text{ cm}^{-1}$) for AN (Fig. 1).

The changes in the macromolecules structure during thermooxidative stabilization under isothermal conditions were investigated by means of IR ATR spectroscopy. To do so, a film specimen was put in a cell of the Netzsch DSC 204 instrument under inert atmosphere and kept at constant temperature during predefined time; the specimen IR ATR spectrum (diamond crystal) was then recorded at room temperature using a Spectrum Two FT-IR Spectrometer instrument (spectral range 4000–600 cm^{-1} , resolution 0.5 cm^{-1}).

The fraction of unreacted nitrile groups φ_{CN} [52] was determined using the following equation

$$\varphi_{\text{CN}} = \frac{A_{\text{C}\equiv\text{N}}}{A_{\text{C}\equiv\text{N}} + fA_{\text{C}=\text{N}-}} \quad (1)$$

with $A_{\text{C}\equiv\text{N}}$ being the absorbance of the nitrile groups $-\text{C}\equiv\text{N}$, $A_{\text{C}=\text{N}-}$ being the absorbance of the imine groups $-\text{C}=\text{N}-$, and f being the ratio of the molar absorptivities equal to 0.29.

RESULTS AND DISCUSSION

Synthesis of Copolymers of Acrylonitrile and Ethyl 2-Cyanoacrylate and Their Characteristics

ECA can be polymerized via the radical as well as anionic mechanism. The latter route is readily realized in the presence of DMSO, and acids are used to suppress anionic polymerization of ECA [31]. The experiment revealed that 0.2 wt % of TSA (with respect to the system containing 60 wt % of DMSO, 20 wt % of AN, and 20 wt % of ECA) could prevent the polymer formation during 24 h. That was enough to prepare the reaction mixtures and perform the radical polymerization.

Estimation of the copolymerization constants of AN and ECA via the $Q-e$ scheme [51] gave $r_{\text{AN}} = 0.07$

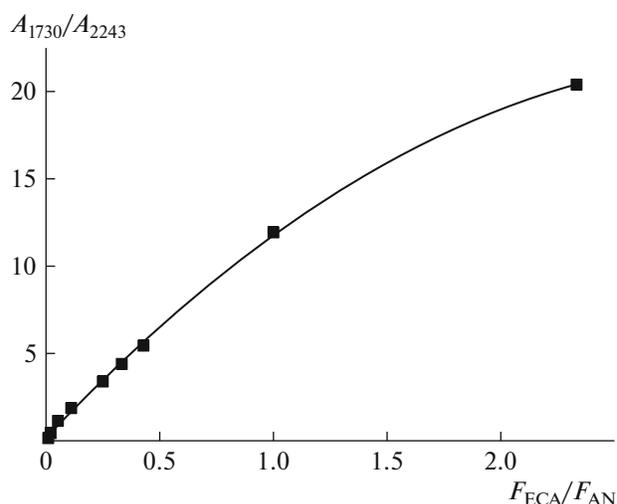


Fig. 1. Calibration curve of the ratio of characteristic absorption bands of the carbonyl (A_{1730}) and nitrile (A_{2243}) groups as a function of the molar content of the ECA (F_{ECA}) and AN (F_{AN}) units in the mixture of the homopolymers for determination of the composition of the AN–ECA copolymer. Color figures are available in the online version.

and $r_{\text{ECA}} = 13.7$, and higher reactivity of ECA in the copolymerization with AN could be expected. Relative activity of AN and ECA in the radical polymerization was determined from the analysis of the composition of copolymers synthesized at low conversion of the monomer mixtures differing in the composition (Fig. 2), by mean of the least squares and [53] and the Fineman–Ross methods [54]. ECA was found three orders more reactive in the copolymerization with AN: $r_{\text{AN}} = 0.052 \pm 0.02$, $r_{\text{ECA}} = 54.5 \pm 7.2$ (least squares method) and $r_{\text{AN}} = 0.042 \pm 0.01$, $r_{\text{ECA}} = 46.7 \pm 11.9$ (the Fineman–Ross method). Hence, ECA was consumed faster than AN, and the copolymer nonuniform in the composition should be formed at high conversion, irrespectively of the monomer mixture composition.

The composition nonuniformity of the copolymer could be eliminated taking advantage of radical polymerization with reversible chain deactivation, for example, RAFT polymerization [55]. Due to huge difference in the monomers reactivity, the macromolecules with gradient structure and high uniformity with respect to molecular mass and composition should be thus formed. To synthesize the copolymers with uniform distribution of the ECA units along the chain, concentration of ECA in the reaction mixture should be tuned during the copolymerization. In view of that, copolymerization of AN and ECA in this study was performed using two methods: 1) AN and ECA were introduced in the reaction mixture prior to the synthesis; 2) ECA was continuously added during the copolymerization (Table 1).

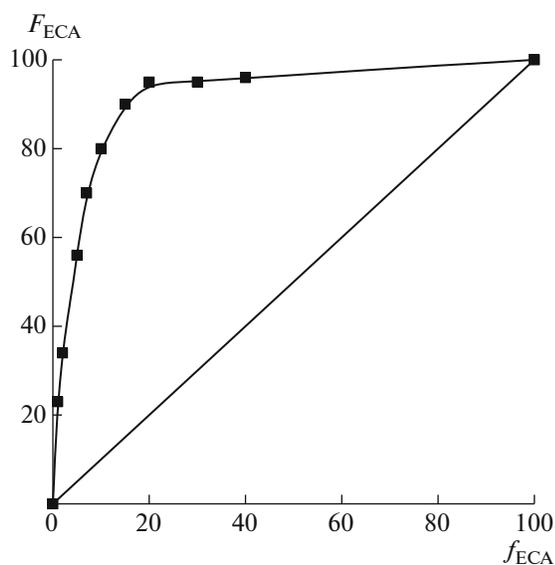


Fig. 2. Diagram of composition of the AN–ECA copolymer formed under conditions of conventional radical copolymerization. F_{ECA} and f_{ECA} are molar fractions of ECA in the copolymer and the monomers mixture (%), respectively.

Irrespective of the method of ECA introduction, the copolymerization occurred without induction period (Fig. 3), and the starting copolymerization rate was increased with the increase in the ECA fraction in the system. The maximum conversion achieved during 4.5 h at 80°C was 55–65%, being increased in the case of the single-portion addition of ECA in comparison with the continuous one.

The main features of the RAFT mechanism are linear increase in the number-average molecular mass M_n and formation of the polymer with narrow MMD. In the case of the considered systems, unimodal MMD of the copolymers (Fig. 4a), linear growth of M_n with conversion (Fig. 4b), and low dispersity of the copolymers $\bar{D} = 1.24\text{--}1.45$ (Fig. 4c) were observed.

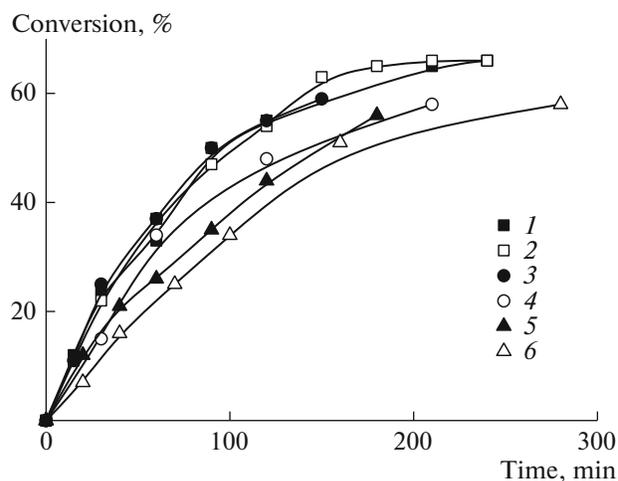


Fig. 3. Conversion as function of duration of copolymerization of AN and ECA in DMSO in the presence of 3×10^{-3} mol/L of AIBN, 3×10^{-3} mol/L of DTMPA, and 0.2 wt % of TSA at 80°C. Method of ECA charging: single portion (1, 2), continuous (3–6); f_{ECA} in the starting mixture 5 (1) and 10 mol % (2); rate of ECA charging 1.12 (3), 0.65 (4), 0.36 (5), and 0.16 mL/h (6).

Preliminary experiments revealed that the copolymers M_n in the studied systems was inversely proportional to the concentration of the RAFT agent. Those results confirmed realization of the RAFT polymerization mechanism and suppression of anionic polymerization of ECA.

Evidently, the method of ECA introduction in the copolymerization should be reflected in the composition of the copolymers formed at different conversion. Figure 5 displays the dependences of the molar fraction of ECA in the copolymer as function of total conversion of the monomers for the conducted experiments. In the case of simultaneous introduction of AN and ECA in the copolymerization, rapid consumption of ECA was observed (curves 1 and 2), due to high dif-

Table 1. Formulations and conditions of synthesis of copolymers of AN and ECA in DMSO under conditions of RAFT polymerization and their parameters

Sample	f_{ECA}^* , mol %	$V_{\text{ECA+DMSO}}$, mL/h	f_{ECA}^{**} , mol %	Conversion, %	$M_n \times 10^{-3}$	\bar{D}	F_{ECA} , mol %
PAN	0	Not introduced	0	55	28.8	1.22	0
1	5	Introduced at once	5	66	29.0	1.24	12.3
2	10	Introduced at once	10	66	32.0	1.23	17.1
3	0	1.12	11.36	55	23.4	1.43	38.2
4	0	0.65	7.18	58	24.0	1.45	17.0
5	0	0.36	4.26	56	23.8	1.33	11.8
6	0	0.16	1.84	58	25.8	1.40	4.7

* Molar fraction of ECA in the starting monomers mixture.

** Molar fraction of ECA introduced in the copolymerization.

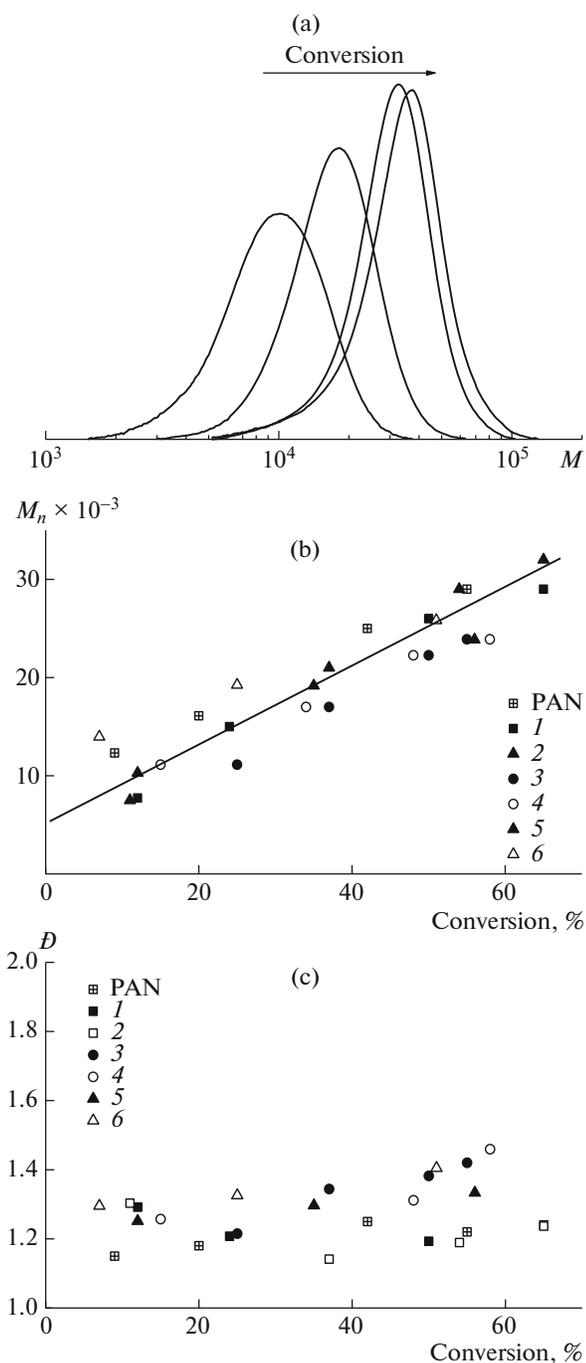


Fig. 4. MMD curves normalized to unity are for the copolymers formed during simultaneous charging of the monomers and $f_{\text{ECA}} = 5$ mol % in the starting mixture at different conversions (a); M_n (b) and dispersity \bar{D} (c) of the AN–ECA copolymers as functions of the conversion. Hereafter the points number correspond to the samples number in Table 1.

ference in the monomers reactivity. The change in the average composition of the copolymer during the copolymerization, along with the RAFT mechanism, pointed at the formation of the gradient copolymer [56]:

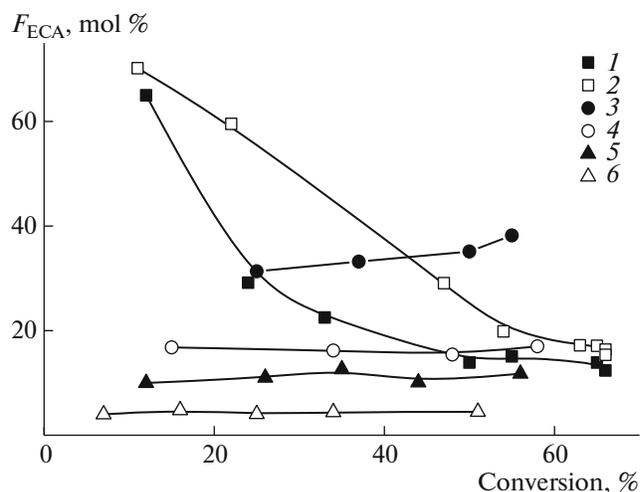


Fig. 5. Molar fraction of ECA in the copolymer F_{ECA} as function of the monomers conversion for the AN–ECA copolymers obtained via RAFT polymerization in DMSO in the presence of $[\text{AIBN}]_0 = 3 \times 10^{-3}$ mol/L, $[\text{DTMPA}]_0 = 3 \times 10^{-3}$ mol/L, and TSA = 0.2 wt % at 80°C.

In the case of continuous introduction of ECA, the copolymer composition remained unchanged during the copolymerization (curves 3–6). Hence, the statistical copolymer uniform in the composition was formed rather than the gradient one:



Higher rate of the ECA introduction increased its fraction in the copolymer. Composition of the copolymers isolated at the limiting conversion is given in Table 1. It is to be seen that the copolymers with the same average composition but differing in the chain microstructure could be obtained by tuning the method and rate of ECA introduction.

We have earlier shown that thermal behavior of AN copolymers, properties of their solutions, and mechanical parameters of the formed fiber depend on the microstructure of the copolymers chain [57]. Similar features were expected in the considered systems.

Investigation of Thermal Behavior of the Copolymers under Inert Atmosphere

Thermal behavior of PAN and poly(ethyl 2-cyanoacrylate) under inert atmosphere is significantly different [18, 49]. Decomposition of poly(ethyl 2-cyanoacrylate) with evolution of the monomer starts at 160°C, the maximum decomposition rate being achieved at ~265°C [43, 49]. Heating of PAN is accompanied by exothermic reaction of intra- and intermolecular cyclization [19] occurring over a nar-

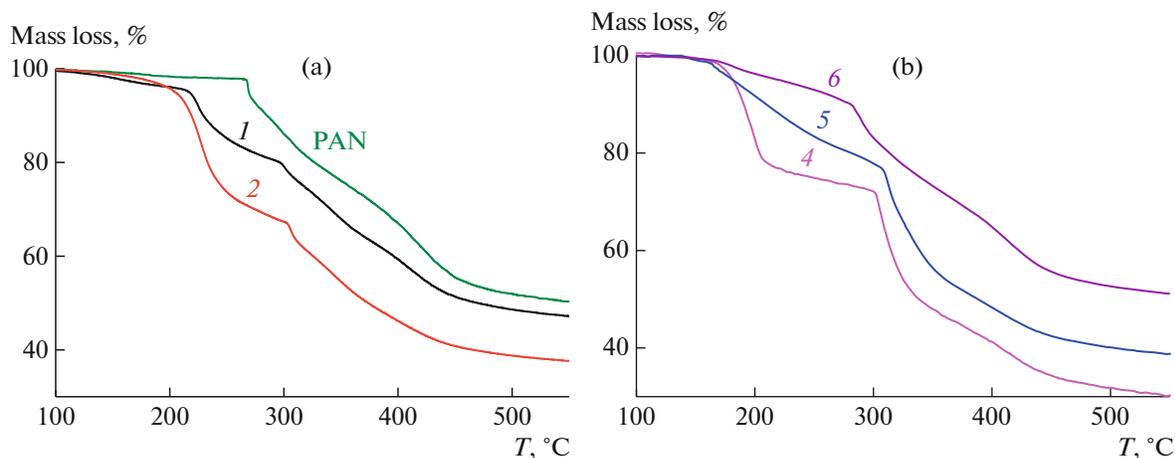


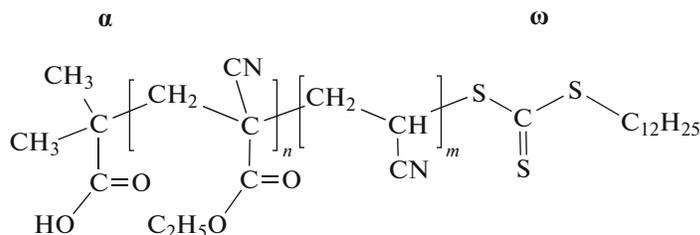
Fig. 7. Mass loss curves for PAN and the AN–ECA copolymers at the heating rate 10 deg/min under argon.

related to depolymerization due to the presence of the ECA units in the copolymer chains.

The TGA analysis of the polymers revealed that heat resistance of the synthesized copolymers depended on the content of ECA and the units distribution along the chain (Fig. 7). Temperature of the mass loss onset of PAN corresponded to the maximum of the exothermic effect in the DSC thermogram. The statistical copolymer with 4.7 mol % of ECA (curve 6) revealed the heat resistance close to that of PAN, yet slight mass loss was observed at temperature above 160°C. Further increase in the fraction of ECA in the statistical copolymers led to practically unchanged temperature of the thermal destruction onset, and the low-temperature stage of the mass loss became noticeable in the thermograms, becoming more prominent with the increase in the fraction of ECA in the copolymer (curves 4 and 5). The decomposition was accompanied by the appearance of characteristic smell of

ECA. Let us notice that the endothermic peak in the DSC curves was observed in that temperature range. In the case of the gradient copolymers, the low-temperature stage of the mass loss was observed at temperature above 200°C. However, in that case the decrease in the ECA fraction in the copolymer led to the increase in the heat resistance of the copolymer (curves 1 and 2).

Let us mention that the gradient copolymers with the longer ECA units sequences in comparison with the statistical copolymers exhibited higher thermal resistance (Table 3). That result could be explained in view of the mechanism of the copolymers formation and analysis of the “weak” bonds in the macromolecules [59]. In the case of the copolymers synthesized under the action of the unsymmetrical trithiocarbonate DTMPA ($C_{12}H_{25}SC(=S)SC(CH_3)_2COOH$), the macromolecules structure could be represented as follows:



In contrast to the polymers obtained via radical or anionic polymerization, the “weak” bond of the macromolecules synthesized via RAFT method is the C–S bond between the terminal monomer unit and the sulfur atom of the trithiocarbonate fragment [60]. Lability of the C–S bond is increased for the quaternary carbon atom in comparison with the tertiary one [60]. Hence, the copolymers with the ω -ter-

minal AN unit should be more heat resistant than these with the α -terminal ECA unit.

In the case of simultaneous charging of the monomers, ECA was rapidly consumed due to its high reactivity, and the macromolecule “head” (chain α -end) was enriched with the units of that monomer. As a result, the acrylonitrile units were more probably found at the macromolecule “tail” (chain ω -end), combining with the trithiocarbonate fragment. In the

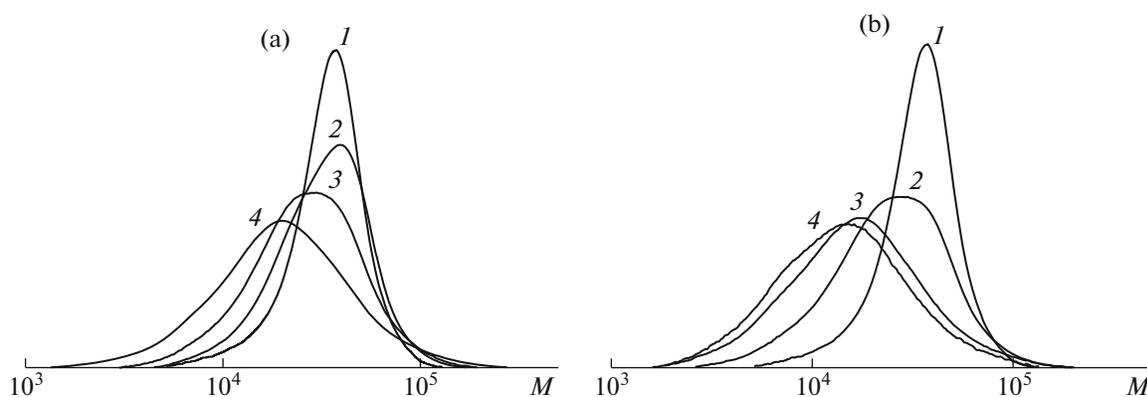


Fig. 8. GPC curves normalized to unity are for copolymer 4 of AN and ECA kept under isothermal conditions at 200 (a) and 225°C (b). Keeping duration: 0 (1), 2 (2), 5 (3), and 10 min (4) (a); 0 (1), 1 (2), 2 (3), and 5 min (4) (b).

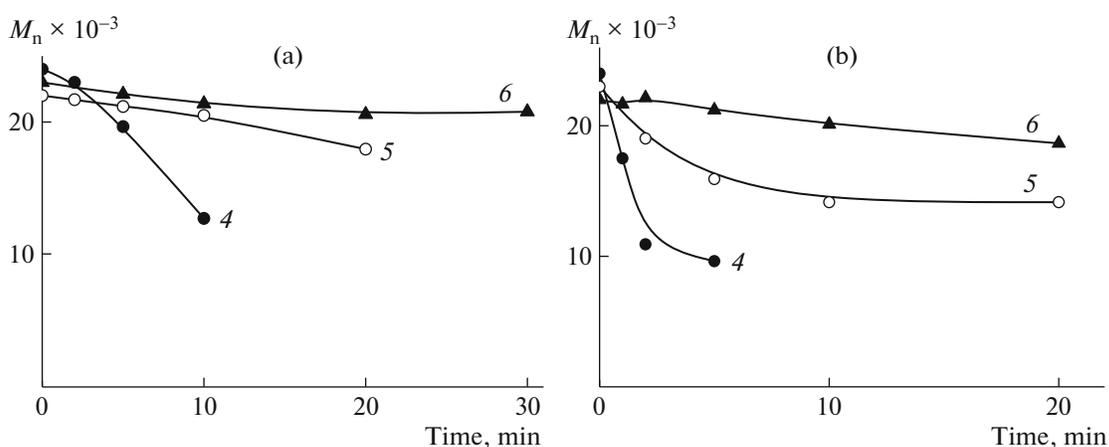


Fig. 9. M_n as function of the duration of isothermal keeping under inert atmosphere at 200 (a) and 225°C (b) of the AN–ECA copolymers with the ECA content 17.0 (4), 11.8 (5), and 4.7 mol % (6).

case of the continuous ECA introduction, probability of its location at the chain ω -end was increased. Hence, the gradient copolymers should indeed be more heat resistant in comparison with the statistical ones.

Table 3. TG results for (co)polymers of AN under inert atmosphere

Sample	T_{10} , °C	T_{20} , °C	T_{30} , °C
PAN	285	327	386
1	230	298	340
2	218	233	275
4	191	204	303
5	209	282	317
6	281	313	371

T_{10} , T_{20} , and T_{30} are temperatures corresponding to loss of 10, 20, and 30% of the mass, respectively.

If the above suggestions on the partial thermal decomposition at 150–250°C were true, isothermal keeping of the copolymers under inert atmosphere should decrease their MM. Indeed, heating of the copolymers at 200 and 225°C led to decrease in their MM. The rate of the MM decrease was increased with the increase in temperature (Fig. 8) and the increase in the fraction of ECA in the copolymer (Fig. 9).

However, partial thermal decomposition does not prevent cyclization of the nitrile groups [58]. The chemical transformations during the copolymers heating were investigated by means of IR spectroscopy. To do so, the polymer films were heated at 225°C under inert atmosphere during different periods.

Figure 10 displays the typical IR spectra of the copolymers before and after the heat treatment. The spectra of copolymers 1 (gradient) and 5 (statistical) contained characteristic absorption bands assigned to the AN and ECA monomer units. The nitrile group stretching $\nu_{C\equiv N}$ of both monomers appeared at 2243 cm^{-1} , whereas stretching ν_{CH} and deformation

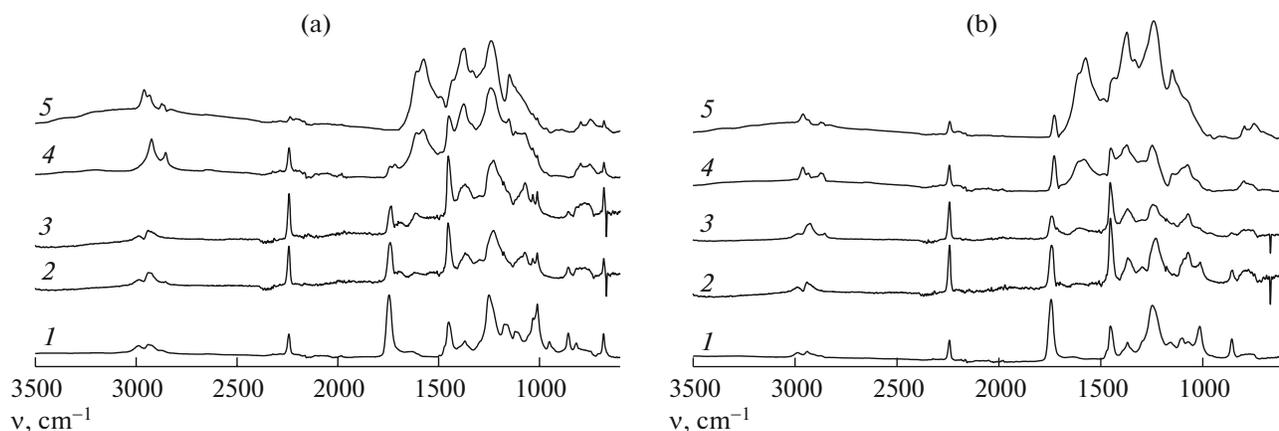


Fig. 10. IR spectra recorded during heat treatment of copolymers 1 (a) and 5 (b) at 225°C. Heat treatment duration 0 (1), 5 (2), 20 (3), 120 (4), and 240 min (5).

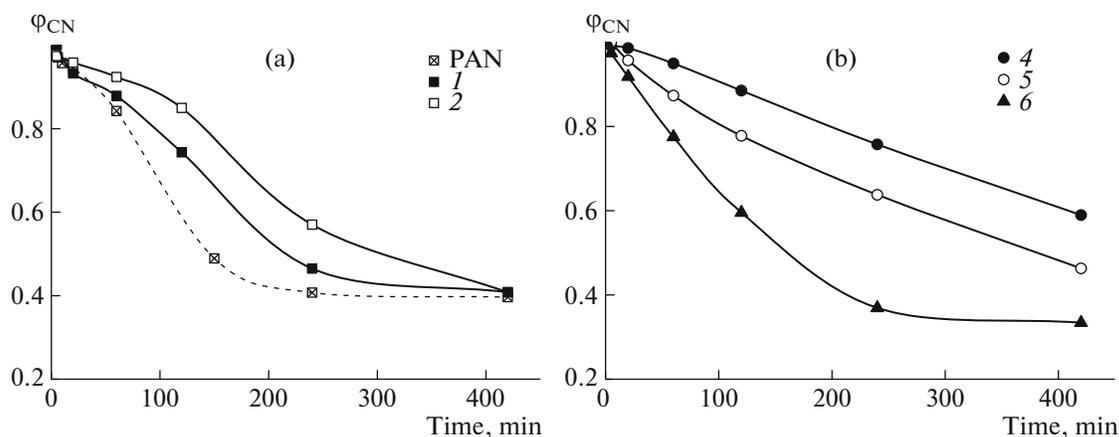


Fig. 11. Total conversion of the nitrile groups as function of duration of isothermal treatment at 225°C under argon atmosphere for the films of the AN–ECA copolymers obtained with single-portion (1, 2) and continuous charging of ECA (4–6).

vibrations δ_{CHH} of the methylene and methine groups of the backbone were observed at 3000–2850 and 1448, 1370 cm^{-1} , respectively. The absorption band of stretching of the C=O group of ECA was observed at 1746 cm^{-1} , and the –C–O– stretching were found at 1300–1100 cm^{-1} . The nitrile groups were converted into the imine ones –CH=N– during the cyclization. That process led to weakening of the absorption band at 2243 cm^{-1} ($\nu_{\text{C}\equiv\text{N}}$) and its broadening followed by splitting into two bands with maximums at 2243 cm^{-1} (the nitrile groups in the starting polymer) and 2200 cm^{-1} (the nitrile group involved in conjugation). Simultaneously, the absorption bands at 1600–1575 cm^{-1} assigned to the pyridine structure were observed. Moreover, novel absorption bands due to the formation of the conjugated bonds system were observed at 3000–2700 and 1600–1000 cm^{-1} [18]. The absorption band at 1746 cm^{-1} assigned to the carbonyl groups $\nu_{\text{C}=\text{O}}$ was simultaneously weakened.

To perform comparative quantitative analysis of the rate of conversion of the nitrile groups, the change in the fraction of unreacted nitrile groups ϕ_{CN} as a function of time (Fig. 11) was calculated using Eq. (1). It is to be seen that the increase in the fraction of ECA in the gradient copolymers (curves 1 and 2) led to the decrease in the overall rate of the copolymer nitrile groups transformation. Similar trend was observed in the case of the statistical copolymers (curves 4–6).

Equation (1) did not account for the fact that weakening of the absorption band of the nitrile groups was due to partial decomposition of the polymer (depolymerization of ECA) in addition to the nitrile groups conversion into the imine ones. Nevertheless, comparison of the copolymers of the same composition differing in the microstructure (1 and 5 or 2 and 4) showed that the cyclization was faster in the case of the gradient copolymers in comparison to the statistical ones.

CONCLUSION

Radical copolymerization of acrylonitrile with ethyl 2-cyanoacrylate was performed for the first time in this study. It was shown that ECA was about three orders of magnitude more reactive than AN in the radical copolymerization. The use of RAFT agent based on nonsymmetrical trithiocarbonate (DTMPA) allowed the synthesis of copolymers with narrow MMD and controllable MM. Due to high difference in the monomers reactivity, rapid consumption of ECA and spontaneous formation of the gradient copolymer occurred in the case of simultaneous monomers charging. As a result, the “head” of the macromolecule was enriched in ECA and the “tail” linked to the trithiocarbonate fragment was enriched in the AN units. Uniform distribution of the ECA units along the chain could be achieved via continuous charging of ECA at a defined rate during the copolymerization. In that case, the probability of the terminal unit linked to the trithiocarbonate fragment to be that of ECA was increased.

The said aspect determined the difference in thermal behavior of gradient and statistical copolymers under inert atmosphere. The gradient copolymers exhibited higher thermal resistance, i.e. their cyclization was likely more probable than depolymerization. The mass loss of the statistical copolymers occurred at lower temperature, and the contribution of the depolymerization was more significant. Irrespectively of the copolymers microstructure, the decrease in the ECA content made their thermal behavior closer to that of AN homopolymer. For example, conversion of the nitrile groups of the statistical copolymer with 4.6 mol % of ECA occurred at approximately the same rate as in the case of PAN.

Hence, copolymers of AN and ECA with low content of the latter (up to 5 mol %) allowed broadening of the temperature range of the cyclization reaction and decrease in the heat evolution intensity. Therefore, such copolymers are promising objects for the production of PAN precursors of carbon fiber.

CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interest.

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