
FUNCTIONAL POLYMERS

Terpolymers of Acrylonitrile, Acrylic Acid, and Alkyl Acrylates: Effect of Alkyl Acrylate on the Thermal Properties of Copolymers

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Abstract—Using asymmetric trithiocarbonate-mediated reversible addition-fragmentation chain transfer polymerization, terpolymers of acrylonitrile with acrylic acid and alkyl acrylate are synthesized; methyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, and lauryl acrylate are used as an alkyl acrylate. The molecular structure of the terpolymers is set by varying composition of the monomer mixture and regime of introducing acrylic acid and alkyl acrylate into the reaction medium, instantaneously or continuously in the course of synthesis, and the molecular weight of the terpolymer is specified by the concentration of trithiocarbonate. Study of the thermal behavior of the synthesized terpolymers shows that the temperature interval of cyclization and the intensity of heat release depend on the amount and molar ratio of acrylic acid to alkyl acrylate. At the molar fraction of acrylonitrile ~90%, the nature of alkyl acrylate insignificantly affects the thermal effect of cyclization of nitrile groups; however, the distribution of acrylic acid and acrylonitrile units in the terpolymer influences the ratio between ionic and radical mechanisms of cyclization. Similar effects are observed in the thermal treatment of the terpolymers in air. An analysis of a change in the chemical structure of the terpolymers upon thermal treatment in an inert atmosphere and in air indicates that lengthening of the alkyl substituent in alkyl acrylate contributes to an increase in the length of the system of conjugated bonds and the effect of chain microstructure on it becomes more pronounced on going from methyl acrylate to lauryl acrylate.

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INTRODUCTION

In recent decades, carbon fibers have been widely used in designing polymer composite materials for various purposes [1–4]. One of the most promising sources for producing carbon fibers is acrylonitrile copolymers [5, 6]. The presence of a cheap raw material and high mechanical properties stipulate an increased interest in these copolymers.

A carbon fiber based on PAN is the product of the multistage process, including the stages of polymer synthesis, fiber spinning, and its thermal treatment. Characteristics of the final product considerably depend on the method and conditions of each stage. For example, the composition of copolymers, the distribution of comonomer units in a chain, the width of MWD, and the compositional heterogeneity that are set during the synthesis influence the properties of acrylonitrile (AN) copolymers at the stages of formation and thermal treatment [7–9].

The low-temperature stage of thermal treatment, referred to as thermal stabilization, leads to development of a ladder structure of the polymer, which is accompanied by an intense heat release [10]. In an inert atmosphere, intramolecular and intermolecular cyclization of PAN units occurs; in air, it is accompanied by oxidation and dehydrogenation reactions [11]. It is desirable to implement these processes in a wide temperature interval; to this end, monomers with carboxyl or amide groups are used which promote a shift in the onset of cyclization to the low-temperature region, as well as (meth)acrylate monomers, which, on the contrary, shift cyclization to high temperatures. The first type of monomers provides the initiation of cyclization by the ionic mechanism [12]. Among carboxylic acids, the most pronounced effect is achieved owing to the use of itaconic and acrylic acids and, to a lesser extent, methacrylic acid [12–15]. (Meth)acry-

late monomers are reckoned to be inert and exert no effect on the radical mechanism of cyclization [16].

Traditional commercial precursors include both binary copolymers of AN with acrylic acid (AA) and AN with methyl acrylate (MA) and ternary copolymers of AN with MA and itaconic acid, as well as a number of other copolymers [13, 16–21]. However, the optimum composition of PAN precursors and its characteristics are still unknown, and this is one of the most controversial issues. Ternary copolymers (terpolymers) are convenient since precursor properties can be tuned in a wide range.

This study addresses terpolymers based on AN, AA, and alkyl acrylates. The bulk of the published data concern only terpolymers with methyl acrylate [17, 18, 22, 23]. Alkyl acrylates with a longer alkyl substituent are not less interesting, since they additionally increase the flexibility of a chain and reduce the glass transition temperature of the copolymer, which makes them promising for spinning processes.

Earlier, we carried out the comparative study of binary copolymers AN-AA and AN-alkyl acrylates and demonstrated that the synthetic procedure (classical or controlled radical polymerization) and the regime of introducing monomer into the synthesis (instantaneous, continuous, and semicontinuous) influence the rheological and thermal properties of the copolymers. For example, at close average compositions of “classical” copolymers, a difference in their compositional heterogeneity entails an unpredictable change in the activation energy of cyclization, degree of stabilization, and heat resistance of copolymers. In contrast, for the copolymers of the same average composition which are synthesized under conditions of reversible addition-fragmentation chain transfer (RAFT), a change in chain microstructure, that is, the distribution of acrylic acid units in a chain, makes it possible to control the rate of cyclization while retaining high heat resistance of the copolymers. As the fraction of AA in a copolymer grows, the activation energy of ionic cyclization decreases, while the activation energy of radical cyclization increases [24]. The lengthening of alkyl acrylate in a binary copolymer, conversely, exerts no effect on the activation energy of radical cyclization [25].

Therefore, in our opinion, the systematic research into effect of the length of alkyl substituent in alkyl acrylate on the thermal properties of terpolymers AN-AA-alkyl acrylate is an urgent task. It is not improbable that the uncovered regularities will make it possible to widen the scope of acrylonitrile copolymers applied in the manufacture of fibers for different purposes.

EXPERIMENTAL

Acrylonitrile (99%), methyl acrylate (MA, 97%), *n*-butyl acrylate (BA, 99%), 2-ethylhexyl acrylate (EHA, 99%), lauryl acrylate (LA, 99%), and acrylic acid (AA, >99%) purchased from Acros were purified via distillation according to the standard technique. Lauryl acrylate (Aldrich) was used without additional purification. AIBN was recrystallized from ethanol and stored in the dark at -3°C . Anhydrous potassium persulfate (PPS, >98%) and RAFT agent, 2-cyano-2-propyldodecyl trithiocarbonate ($\text{CN}(\text{CH}_3)_2\text{C}-\text{S}-\text{C}(=\text{S})-\text{S}-\text{C}_{12}\text{H}_{25}$, CTC, 97%, Aldrich), were used as received. DMSO (99%) and DMF (HPLC) purchased from Fluka were distilled before use.

To prepare samples, the RAFT agent was dissolved in AN (1×10^{-3} mol/L concentration in the final reaction mixture), AA and alkyl acrylate were added at the specified ratio, and the initiator solution in DMSO (5×10^{-4} or 1×10^{-3} mol/L in the final reaction mixture) was prepared. The resultant solutions were mixed at monomer : solvent (2 : 3, vol/vol), and the finished mixtures were poured in ampoules that were connected to a vacuum setup and outgassed via four freeze-thaw-pump cycles. Once a residual pressure of 5×10^{-3} mmHg was attained, the ampoules were sealed.

Polymerization was carried out at 80°C ; when polymerization was complete, the ampoules were cooled to room temperature and opened and, if necessary, the polymerization product was dissolved in DMSO. Solutions were precipitated in deionized water under continuous stirring, and the isolated polymer was filtered, washed with water, and vacuum dried to a constant weight. The conversion of the sample was determined gravimetrically.

The molecular weight characteristics of AN copolymers were investigated by gel permeation chromatography on a PolymerLab GPC-120 chromatograph equipped with two PLgel 5 μm MIXED C columns ($M = (5 \times 10^2) - (1 \times 10^7)$). Analysis was carried out at 50°C in DMF containing 0.1 wt % LiBr (flow rate, 1 mL/min) using a polymer solution in the eluent with a polymer concentration not above 1 mg/mL and no less than 0.7 mg/mL. MW was calculated according to PMMA standards; for acrylonitrile copolymers, MW was recalculated using the well-known Kuhn-Mark-Houwink coefficients ($K_{\text{PAN}} = 39.4 \times 10^{-4}$ and $\alpha = 0.75$; $K_{\text{PMMA}} = 17.7 \times 10^{-4}$ and $\alpha = 0.62$ [26]).

Before studying the copolymers, a 4% polymer solution in DMSO was prepared. It was poured on a glass horizontal substrate, and the solvent was evaporated at 80°C until a constant weight was achieved.

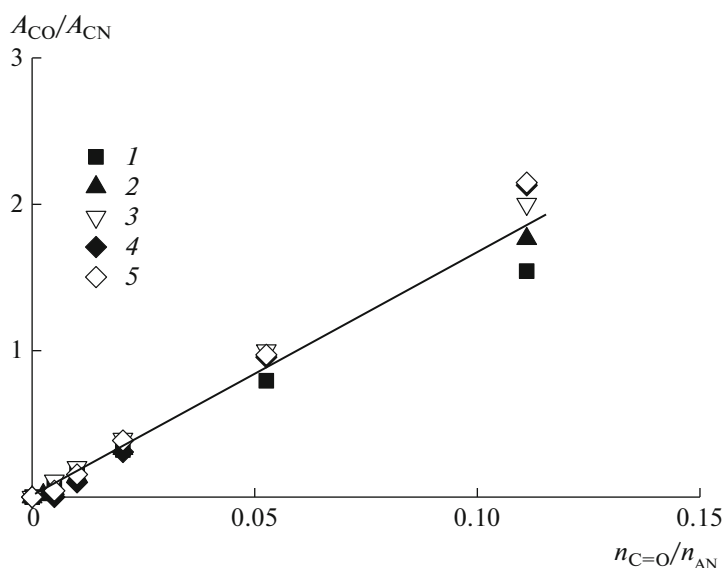


Fig. 1. Initial sections of calibration plots for AN mixtures with (1) AA, (2) MA, (3) BA, (4) EHA, and (5) LA used to determine the composition of copolymers by IR spectroscopy.

The finished films were removed from the substrate, and the square samples with dimensions of 40 mm × 40 mm were cut; the thickness of the film was 10–15 μm.

Thermal effects observed in the dynamic heating of copolymer films were studied on a Netzsch DSC 204 differential scanning calorimeter (Netzsch, Germany) in an atmosphere of dry gas (air, argon) at a flow rate of 100 mL/min in the range of 30–450°C. Measurements were conducted at a heating rate of 5–20°C/min in an air atmosphere and at a heating rate of 10°C/min under an inert atmosphere; the film with a weight of 4–6 mg was placed in a standard aluminum crucible without a cover. The results were treated by means of the Netzsch Proteus program.

The activation energy of cyclization E_a was determined by the Kissinger method [27]

$$-\frac{E_a}{R} = \frac{d \left[\ln \left(\frac{\phi}{T_p^2} \right) \right]}{d \left(\frac{1}{T_p} \right)}, \quad (1)$$

where R is the universal gas constant, T_p is the temperature of the exothermic peak (K), and ϕ is the rate of heating (°C/min).

The composition of PAN copolymer films was studied by ATR FTIR spectroscopy using a PerkinElmer Spectrum Two FTIR Spectrometer in the range of 4000–400 cm⁻¹. Bands due to functional groups, the carbonyl groups of acrylic acid and ester (1715–1728 cm⁻¹ depending on alkyl acrylate) and the nitrile group of acrylonitrile (2229 cm⁻¹), were used as characteristic bands. The intensity of characteristic

absorption bands was determined, and the composition of the copolymer was calculated from the calibration plots derived from dependence of the ratio of intensity of absorption bands corresponding to the carbonyl group and the nitrile group on the molar ratio of acrylate monomer and acrylonitrile.

Since resolution of IR signals corresponding to the carbonyl groups of ester and acrylic acid is hardly possible, the molar ratio between AN and acrylic comonomer (AA and alkyl acrylate) units was assessed. In the tested composition interval, the calibration dependences of AN/AA, AN/MA, AN/BA, AN/EHA, and AN/LA are close to each other (Fig. 1); therefore, the molar ratio of AN : acrylic comonomer units can be determined with a sufficient accuracy.

Changes in the structure of macromolecules during cyclization were investigated by ATR IR spectroscopy. For this purpose, the film sample was heated at 250°C under argon for the specified time and FTIR spectra were measured at room temperature in the ATR mode (diamond crystal) in the range from 4000 to 600 cm⁻¹ on a PerkinElmer Spectrum Two FTIR Spectrometer with an IR microscope at a resolution of 0.5 cm⁻¹.

The fraction of unreacted nitrile groups ϕ_{CN} [28] and the degree of stabilization E_s [29] were calculated by equations

$$\phi_{CN} = \frac{A_{2240 \text{ cm}^{-1}}}{A_{2240 \text{ cm}^{-1}} + fA_{1590 \text{ cm}^{-1}}}, \quad (2)$$

$$E_s = \frac{A_{1590 \text{ cm}^{-1}}}{A_{2240 \text{ cm}^{-1}}}, \quad (3)$$

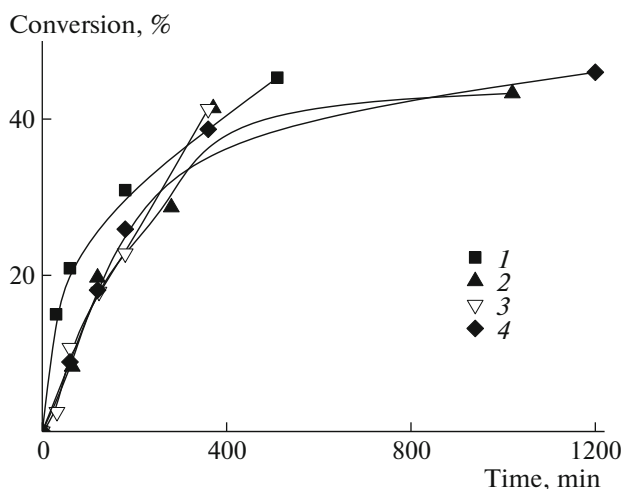


Fig. 2. Time dependence of conversion for the copolymerization of systems AN-AA-alkyl acrylate: (1) MA, (2) BA, (3) EHA, and (4) LA in DMSO in the presence of CTC and AIBN. Here and in Figs. 3 and 4, $T = 80^{\circ}\text{C}$; weight ratio of monomers, 40%; $[\text{AIBN}]_0 = 5 \times 10^{-4} \text{ mol/L}$; $[\text{CTC}]_0 = 10^{-3} \text{ mol/L}$; and AN : AA : alkyl acrylate = 93 : 7 : 3.5.

where $A_{2240 \text{ cm}^{-1}}$ is the intensity of absorption due to nitrile groups $\text{C}\equiv\text{N}$, $A_{1590 \text{ cm}^{-1}}$ is the intensity of absorption due to imine groups $\text{C}=\text{N}-$, and f is the ratio of molar absorption coefficients equal to 0.29 [28].

RESULTS AND DISCUSSION

Synthesis of Ternary Copolymers

Earlier, it was shown that AN is a more active monomer in RAFT copolymerization with alkyl acrylates (MA, BA, EHA, and LA) in DMSO [25] but is less active in RAFT copolymerization with AA [30]. Therefore, in binary copolymers with alkyl acrylates, the molar fraction of AN in the copolymer remains almost unchanged with an increase in the conversion of monomers at the content of AA in the monomer mixture above 80 mol %, while in copolymers with AA it decreases at the content of AN in the mixture above 90 mol %.

The incorporation of AA units in PAN contributes to widening of the temperature interval of cyclization and decrease in the intensity of heat release owing to realization of an additional ionic mechanism of cyclization initiation [31]. Alkyl acrylates function as an internal plasticizer and deteriorate the regularity of PAN chains, shifting the process of cyclization to high

temperatures and decreasing the intensity of heat release. Hence, the properties of the resultant AN terpolymers can be varied in a wide range by changing the composition of the monomer mixture.

Ternary copolymers were synthesized under conditions chosen for the synthesis of binary copolymers AN-AA [24, 30] and AN-alkyl acrylate [25], and the ratio of the monomers was varied. For example, initially at the fixed molar ratio AN : AA (98 : 2, 95 : 5, 93 : 7, and 90 : 10%), the shortage and equimolar ratio AA : alkyl acrylate were taken. Preliminary experiments showed that, for terpolymers synthesized at ultimate conversions, lengthening of the alkyl substituent in alkyl acrylate causes an increase in the width of MMD of reaction products from $\bar{D} = 1.4\text{--}1.5$ for MA to $\bar{D} = 1.6\text{--}1.7$ for LA. An increase in the fraction of alkyl acrylate relative to AA in the monomer mixture promotes a rise in ultimate conversion by 5–10% and, as a result, causes a small increase in the molecular weight of the polymer.

To prove implementation of the RAFT mechanism in the systems under study, we chose the system with the initial molar ratio of monomers in the mixture AN : AA = 93 : 7 and AA : alkyl acrylate = 2 : 1 (89.8 mol % AN, 6.8 mol % AA, and 3.4 mol % alkyl acrylate). Figure 2 shows time dependences of comonomer conversion for the AIBN-initiated terpolymerization. It is seen that, at the same composition of the monomer mixture, the nature of alkyl acrylate has almost no effect on the kinetics of copolymerization, except MA (curve 1).

The resulting terpolymers are characterized by a unimodal MWD; as conversion increases, the MWD curves shift to high molecular weights (Fig. 3). The molecular weight of terpolymers linearly depends on the conversion of monomers for all the tested systems (Fig. 4a). Note that the terpolymers are characterized by a narrow MWD: molecular weight dispersity is 1.2–1.4 (Fig. 4b). The observed features are typical of the RAFT process.

In accordance with [30], a change in the way of introducing monomers into the reaction medium (instantaneous, semicontinuous, or continuous) does not affect implementation of the RAFT mechanism [30]. We carried out two series of experiments using the monomer mixture of the following molar composition: AN : AA : alkyl acrylate = 98 : 2 : 10.9 (88.4 mol % AN, 1.8 mol % AA, and 9.8 mol % alkyl acrylate): in the first series, the monomers were instantaneously introduced into polymerization, while in the second series, AA and alkyl acrylate were continuously introduced during polymerization. The way of introducing monomers exerts no effect on the initial rate of PPS-initiated RAFT copolymerization

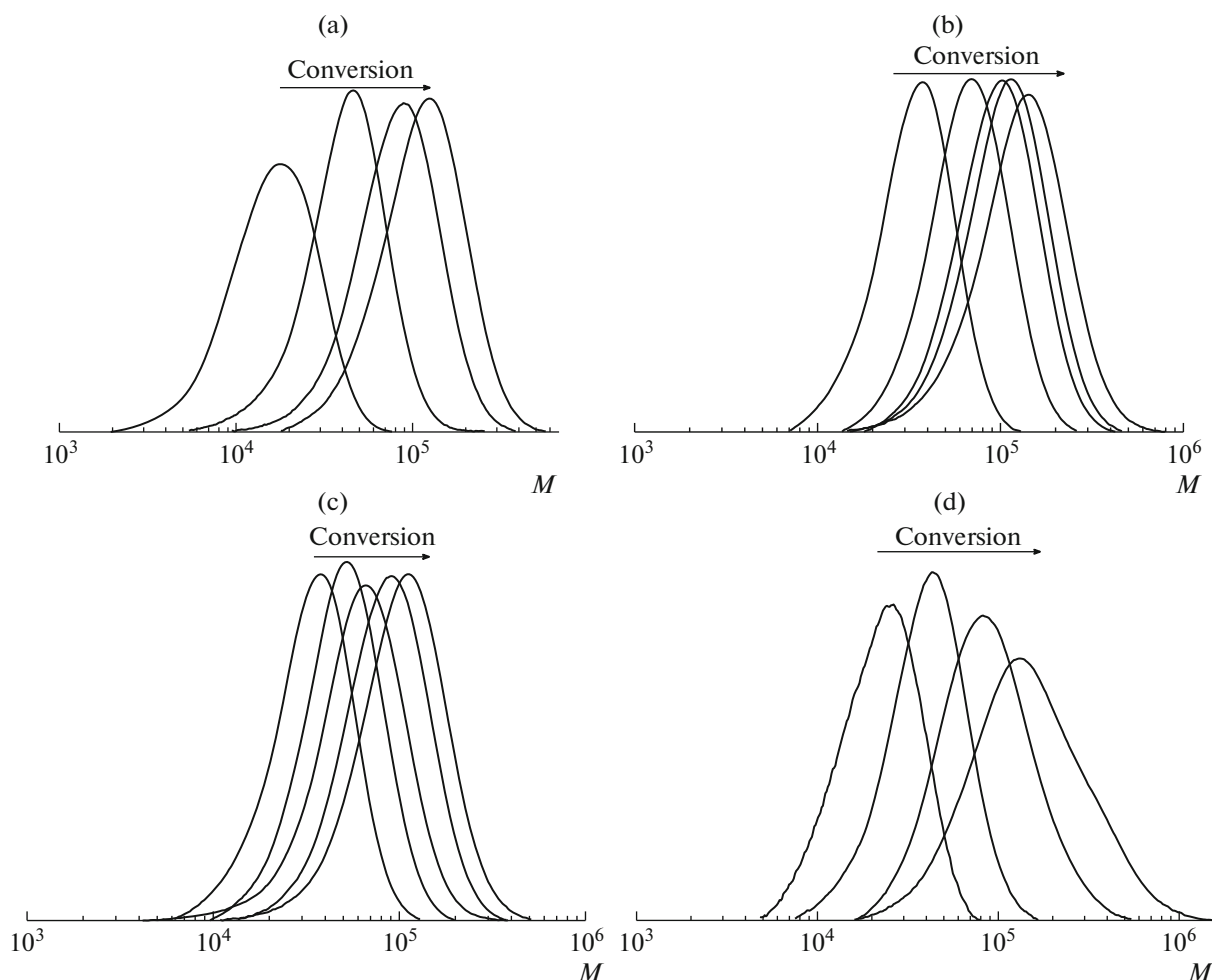


Fig. 3. Unit area normalized GPC curves of terpolymers synthesized by RAFT copolymerization in the system AN-AA-alkyl acrylate: (a) MA, (b) BA, (c) EHA, and (d) LA.

but leads to a small change in the ultimate conversion (Fig. 5).

As is seen from Fig. 6, with an increase in the conversion of monomers, the GPC curves of the copolymers shift to high MW values. The way of introducing monomers into copolymerization affects the MWD of final polymerization products: in the instantaneous introduction regime, higher conversions and, as a consequence, higher molecular weights can be reached. Simultaneously, a rise in viscosity causes a certain broadening of MWD (Table 1). Thus, as expected the RAFT mechanism is also implemented with a change in the way of introducing monomers into synthesis.

The composition of the terpolymers and its evolution during synthesis were studied by ATR FTIR spectroscopy. The IR spectra of the terpolymers show characteristic absorption bands due to AN, AA, and alkyl acrylates. The stretching vibrations of backbone protons are observed in the range of 3000–2840 cm^{-1} ; the vibrations of methylene groups CH_2 manifest

themselves at 2939 ($\nu_{\text{s C-H}}$) and 2875 cm^{-1} ($\nu_{\text{as C-H}}$) and the vibrations of methine groups CH are observed at $\sim 2970 \text{ cm}^{-1}$. Stretching vibrations of nitrile groups

Table 1. Characteristics of terpolymers AN-AA-alkyl acrylate synthesized in the presence of CTC from the monomer mixture AN : AA : alkyl acrylate = 98 : 2 : 10.9

Alkyl acrylate	Regime of introducing monomers	Conversion, %	$M_n \times 10^{-3}$	\bar{D}
MA	Instantaneous	52	53.3	1.66
	Continuous	47	49.9	1.53
BA	Instantaneous	61	60.6	1.70
	Continuous	51	53.2	1.60
LA	Instantaneous	50	44.7	1.65
	Continuous	45	38.5	1.72

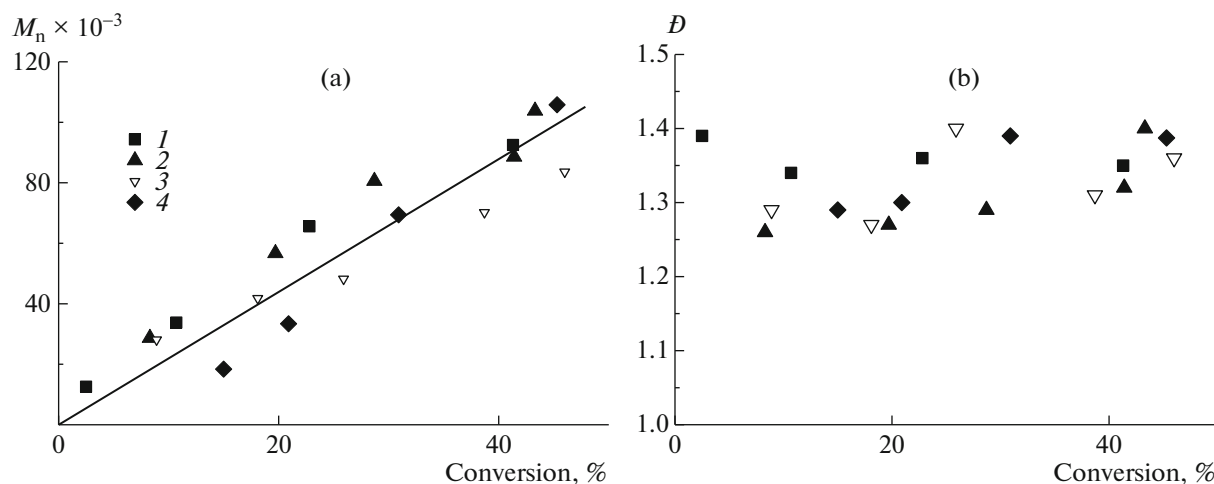


Fig. 4. Plot of (a) M_n and (b) dispersion D as a function of conversion for terpolymers formed by copolymerization in the system AN–AA–alkyl acrylate: (1) MA, (2) BA, (3) EHA, and (4) LA.

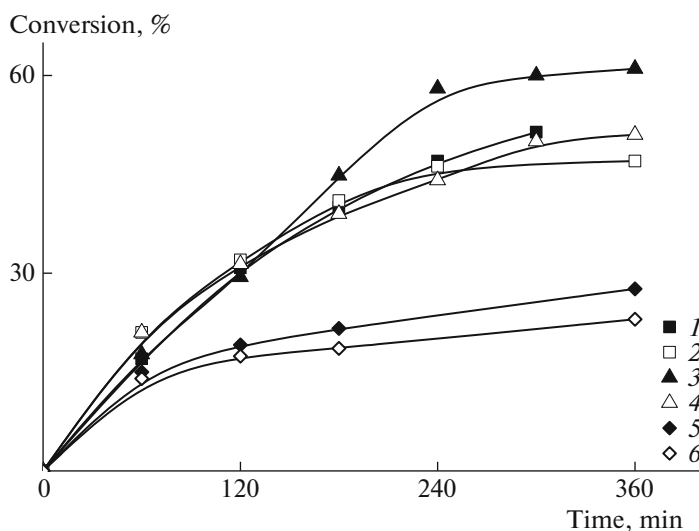


Fig. 5. Time dependence of conversion for systems AN–AA–alkyl acrylate: (1, 2) MA, (3, 4) BA, and (5, 6) LA in DMSO at 55°C in the presence of $[PPS] = [CTC] = 10^{-3}$ mol/L. AN : AA : alkyl acrylate = 98 : 2 : 10.9; the weight content of monomers is 40%; (1, 3, 5) instantaneous and (2, 4, 6) continuous introduction of AA and alkyl acrylate.

of AN ν_{CN} are seen at 2242 cm^{-1} ; stretching vibrations of a carbonyl group $\nu_{C=O}$ in alkyl acrylate are at 1728, 1725, 1726, and 1727 cm^{-1} for MA, BA, EHA, and LA, respectively. Bending vibrations δ_{CHH} are manifested at 1455 and 1357 cm^{-1} , mixed δ_{CHH} and rocking γ_{CH_2} vibrations are detected at 1057 cm^{-1} , and weak absorption bands are observed at 1247 and 762 cm^{-1} [17, 32]. Stretching vibrations of an ester group are seen at 1170 – 1150 cm^{-1} . In the case of MA, a 3000 cm^{-1} shoulder corresponds to the stretching vibrations of CH moieties (group CH_3O) and bands in the range of 750 – 960 cm^{-1} are due to vibrations of methyl and

methylene substituents of the ester group. With an increase in the length of the alkyl substituent, the intensity of absorption bands corresponding to the CH_2 group grows and transition from the general envelope to splitting into separate bands occurs.

Vibrations of OH groups in the carboxyl moiety and bound water manifest themselves as a broad band in the range of 3000 – 3500 cm^{-1} . The band corresponding to the carboxyl group of AA is observed as a shoulder at $\sim 1710\text{ cm}^{-1}$; its intensity increases with increasing fraction of AA in the monomer mixture.

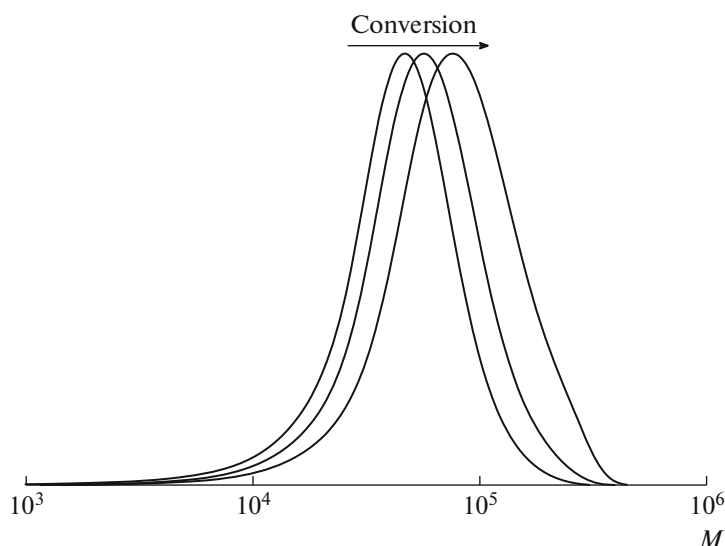


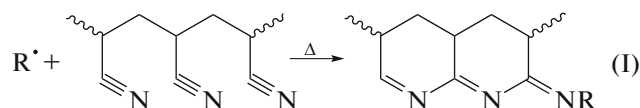
Fig. 6. Unit area normalized GPC curves of terpolymers AN-AA-BA synthesized with the continuous introduction of AA and BA into copolymerization at different conversions in the presence of CTC and PPS.

As is seen from Fig. 7a, for the terpolymers synthesized from the mixture with a molar ratio of components AN : AA : alkyl acrylate of 93 : 7 : 3.5 and containing MA, BA, and EHA, the fraction of AN in the terpolymer does not change during copolymerization. In the case of the terpolymer containing LA, the fraction of AN in the terpolymer grows, and at conversions above 40%, it becomes equal to the value for the terpolymers with other alkyl acrylates. For the terpolymers with the molar ratio of components AN : AA : alkyl acrylate = 98 : 2 : 10.9, the fraction of AN in the terpolymer is invariable up to conversion of ~40% and afterwards the content of AN in the terpolymer decreases gradually.

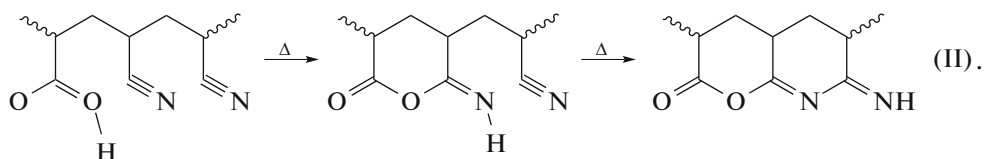
Thus, the terpolymers synthesized at high conversions are characterized by a similar content of AN but different AA : alkyl acrylate ratios.

Thermal Behavior of Acrylonitrile Terpolymers

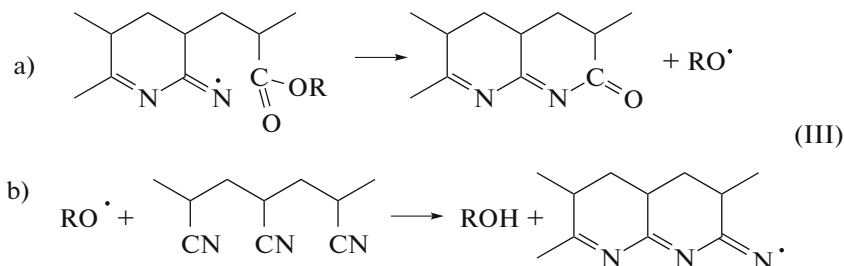
Cyclization reactions occurring in the inert atmosphere. Figure 8 shows the thermograms of copolymers AN, AA, and MA of various composition in the inert atmosphere. It is seen that, at a low content of AA in the copolymer (AN : AA = 98 : 2), the thermograms display one peak which corresponds to the cyclization of AN according to the radical mechanism.



With an increase in the fraction of AA in the copolymer (AN : AA = 93 : 7 or above), the second peak appears on the thermograms which is related to the low-temperature cyclization of AN according to the ionic mechanism:



Units of alkyl acrylate, in this case MA, disturb development of the ladder structure owing to their involvement in the reaction of chain transfer:



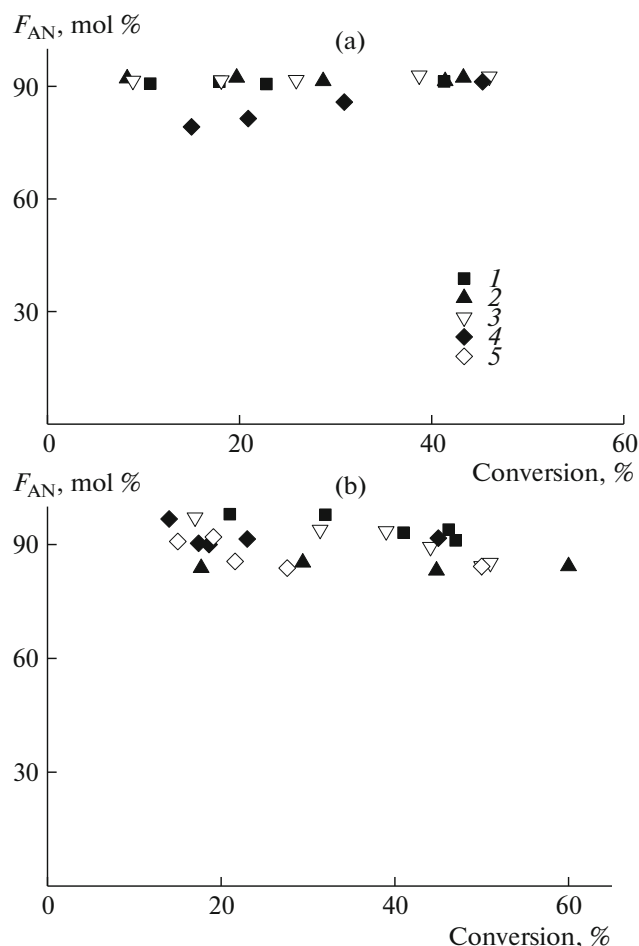


Fig. 7. Conversion dependence of composition of the terpolymers AN-AA-alkyl acrylate at a molar ratio of monomers in the monomer mixture of AN : AA : alkyl acrylate = (a) 93 : 7 : 3.5 and (b) 98 : 2 : 10.9. (a) (1) MA, (2) BA, (3) EHA, and (4) LA; (b) (1) MA, (2, 3) BA, and (4, 5) LA; (1, 2, 4) instantaneous and (3, 5) continuous introduction of monomers.

As a result, the combined introduction of MA and AA units into PAN leads to widening of the temperature interval of cyclization, shift in the maximum temperature of the exo effect to low or high temperatures depending on the AA : MA ratio, and reduction in the thermal effect with an increase in the fraction of MA in the terpolymer (Table 2). Similar effects are observed upon the replacement of MA with other alkyl acrylates.

The effect of the nature of alkyl acrylate on the process of cyclization in the inert atmosphere was investigated using terpolymers synthesized at the ultimate conversion from the monomer mixture containing 89.8 mol % AN, 6.8 mol % AA, and 3.4 mol % alkyl acrylate; their characteristics are listed in Table 3.

Figure 9 presents the thermograms of the terpolymers measured in the inert atmosphere. It is seen that the nature of the alkyl substituent in alkyl acrylate has almost no effect on the thermal behavior of the terpolymers. In the inert atmosphere, the thermograms exhibit two peaks related to cyclization according to ionic and radical mechanisms. The maximum temperature of the peaks on the thermogram, the thermal effect, and its intensity are almost the same for all the tested samples except terpolymer T-MA (Table 4). The glass transition temperature of the terpolymers decreases with increasing length of the alkyl substituent.

The activation energy of cyclization reactions was estimated using the approach advanced by Kissinger [27]. Figure 9b shows as an example the thermograms of T-MA measured at different heating rates. The thermograms were analyzed using Eq. 1 (Fig. 9c), and the activation energies were calculated (Table 4). It is clear that the activation energy of ionic cyclization is independent of the nature of alkyl acrylate and coincides within the accuracy of the experiment. Taking into account that the terpolymers were synthesized from the monomer mixture of the same composition and the content of AN in the terpolymers is similar, it can be assumed that the fraction of AA in the terpolymers is also the same. The activation energies of ionic cyclization of the terpolymers and binary copolymers AN-AA containing ~7 mol % AA are similar [24]. Thus, alkyl acrylate has no effect on ionic cyclization.

In contrast, the activation energy of radical cyclization in the terpolymers depends on the nature of alkyl acrylate and increases with lengthening of the alkyl substituent in alkyl acrylate. In the case of binary copolymers AN-alkyl acrylate with the same content of AN, this dependence is absent [25]. This apparent contradiction is evidently related to different chain microstructure of the polymers. In the case of binary copolymers AN-alkyl acrylates, their composition remains almost unchanged during copolymerization. In the synthesis of terpolymers, AA is a more active monomer than AN [26], and, according to rough estimates of reactivity ratios through the Q-e scheme [26], the activity of AA in copolymerization with acrylates changes in the sequence MA < BA < EHA < LA. In turn, the activity of AN in copolymerization with acrylates grows in the same sequence [25]. Hence, it can be expected that the terpolymers will have a gradient structure, and with an increase in the length of alkyl in alkyl acrylate, the degree of the gradient level will grow. This should result in a change (in this case, reduction) in the length of the sequence of AN units along a chain, and this effect becomes more pronounced on going from MA to LA. Unfortunately, the experimental verification of this assumption is hardly possible because of a relatively low content of the acrylate monomer in the copolymer. This consideration is indirectly confirmed by the fact that, with an increase

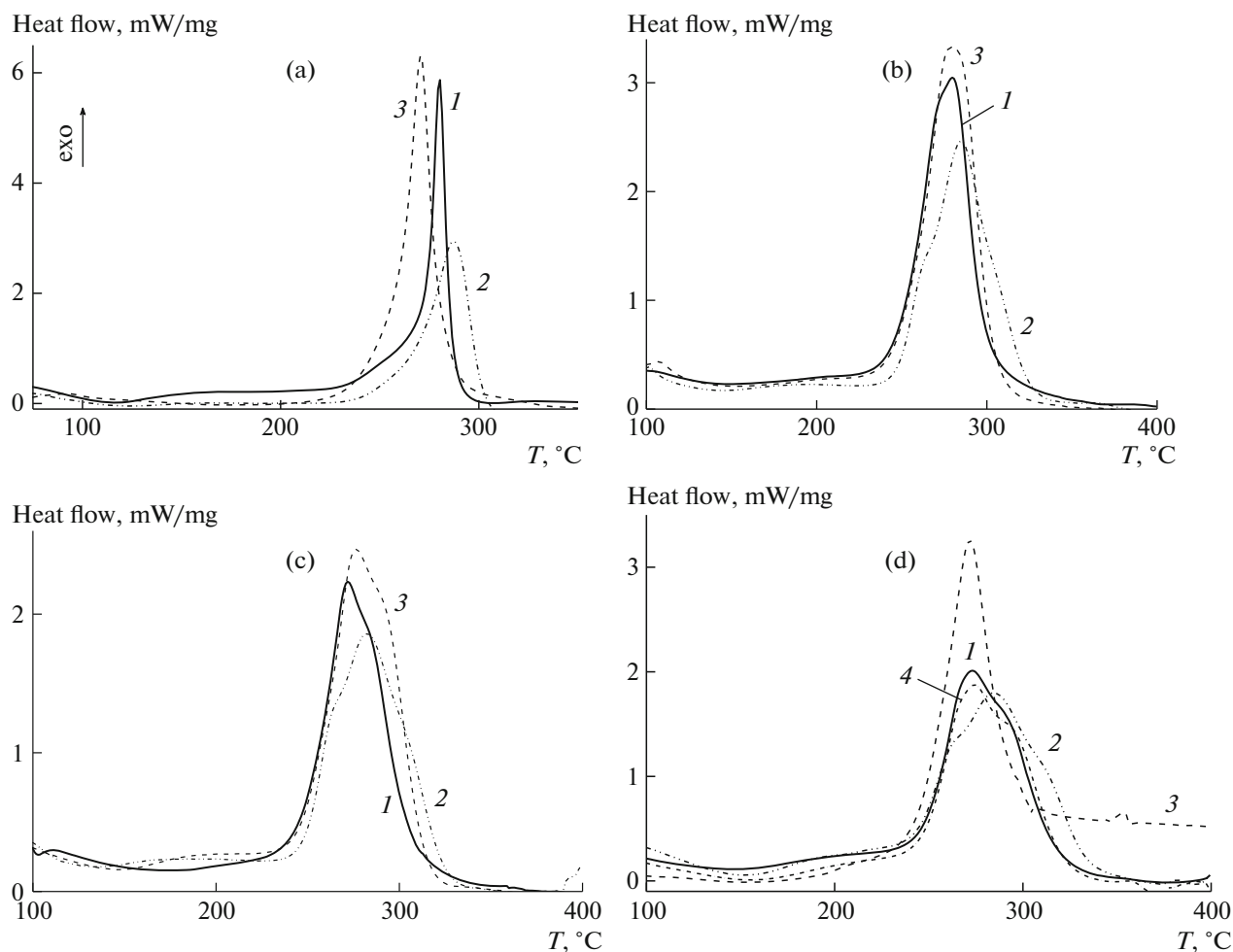


Fig. 8. Thermograms of copolymers AN–MA–AA measured in inert atmosphere at a heating rate of 10°C/min. AN : AA = (a) 98 : 2, (b) 95 : 5, (c) 93 : 7, and (d) 90 : 10; AA : MA = (a) (1) 2 : 0, (2) 2 : 2, and (3) 2 : 1; (b) (1) 5 : 0, (2) 5 : 5, and (3) 5 : 1; (c) (1) 7 : 0, (2) 7 : 3.5, and (3) 7 : 1.4; and (d) (1) 10 : 0, (2) 10 : 5, (3) 10 : 2, and (4) 10 : 1.

in the size of the alkyl substituent, the maximum temperature of the peak corresponding to ionic cyclization remains almost unchanged and the maximum temperature of the peak responsible for radical cyclization shifts to high temperatures.

If the above assumption is true, then a change in the chain microstructure will influence the thermal behavior of the terpolymers. Actually, as is seen from Fig. 10, with the instantaneous introduction of monomers (the initial mixture contains 88.4 mol % AN, 1.8 mol % AA, and 9.8 mol % alkyl acrylate), the intensity of heat release related to ionic cyclization is higher, while the intensity of heat release related to radical cyclization is lower compared with the continuous introduction of AA and alkyl acrylates. In the former case, the temperature interval of cyclization is wider and the heat flow is more uniform compared with the latter case (Table 5). Upon a change in the regime of introducing AA and AN, a more active AA

(compared with AN and acrylates) is consumed more uniformly with its continuous introduction into the synthesis and the rate of initiation of ionic cyclization decreases, while the contribution of the radical mechanism increases. It appears that the continuous introduction of alkyl acrylates facilitates their more uniform involvement in copolymerization; as a result, differences between the thermal behavior of terpolymers with different alkyl acrylates become less distinct. A comparison of Tables 4 and 5 indicates that, at an almost equal content of AN in the terpolymer, the temperature interval of cyclization and close values of the thermal effect may be attained by increasing the fraction of either AA or alkyl acrylate in the copolymer.

Chemical transformations proceeding during the cyclization of terpolymers can be traced using IR spectroscopy. Taking into account the DSC data the films of terpolymers synthesized from the mixture

Table 2. Analysis of thermograms of terpolymers AN-AA-alkyl acrylate of various composition

AN : AA : alkyl acrylate	Content of monomers in the mixture, mol %			Alkyl acrylate	T_{peak} , °C	$-\Delta H$, J/g
	AN	AA	alkyl acrylate			
98 : 2 : 2	96.0	2.0	2.0	MA	287	479
	97.0	2.0	1.0	BA	282	596
				LA	284	566
98 : 2 : 1				MA	270	718
				BA	282	690
				LA	283	600
95 : 5 : 5	90.4	4.8	4.8	MA	285	589
	94.0	5.0	1.0	BA	261, 292	546
				LA	262, 291	547
95 : 5 : 1				MA	279	686
				BA	278	766
				LA	267, 286	686
93 : 7 : 3.5	89.8	6.8	3.4	MA	263, 282	490
	91.7	6.9	1.4	BA	261, 289	495
				LA	263, 279, 293	574
93 : 7 : 1.4				MA	276, 290	573
				BA	271, 285	643
				LA	264, 276, 292	826
90 : 10 : 5	85.7	9.5	4.8	MA	262, 284	578
90 : 10 : 2	88.2	9.8	2.0	MA	272	489
90 : 10 : 1	89.0	10.0	1.0	MA	274, 290	515

containing 89.9 mol % AN, 6.8 mol % AA, and 3.4 mol % alkyl acrylate were heated at 250°C for different times. An analysis of changes in the spectra

Table 3. Characteristics of terpolymers AN-AA-alkyl acrylate synthesized from the monomer mixture containing 89.8 mol % AN, 6.8 mol % AA, and 3.4 mol % alkyl acrylate

Sample	$M_n \times 10^{-3}$	D	F_{AN} , mol %
T-MA	75.9	1.38	91.1
T-BA	95.5	1.42	91.7
T-EHA	74.9	1.40	91.9
T-LA	101.2	1.68	91.2

makes it possible to correlate structural changes in macromolecules with thermal effects observed on thermograms. Figure 11 shows the ATR FTIR spectra of terpolymers T-MA, T-BA, T-EHA, and T-LA before and after heat treatment.

During cyclization, the nitrile group is converted into the imine one. This causes a reduction in the intensity of the absorption band at 2243 cm^{-1} ($\nu_{\text{C}\equiv\text{N}}$) corresponding to stretching vibrations of the nitrile group and its widening at the initial step and then splitting into two bands with maxima at 2243 cm^{-1} (nitrile group in the initial polymer) and at 2200 cm^{-1} (nitrile group involved in conjugation). Simultaneously the absorption band due to $\nu_{\text{C}=\text{N}}$ is detected at $1580\text{--}1590 \text{ cm}^{-1}$, which corresponds to formation of the conjugation system owing to the occurrence of

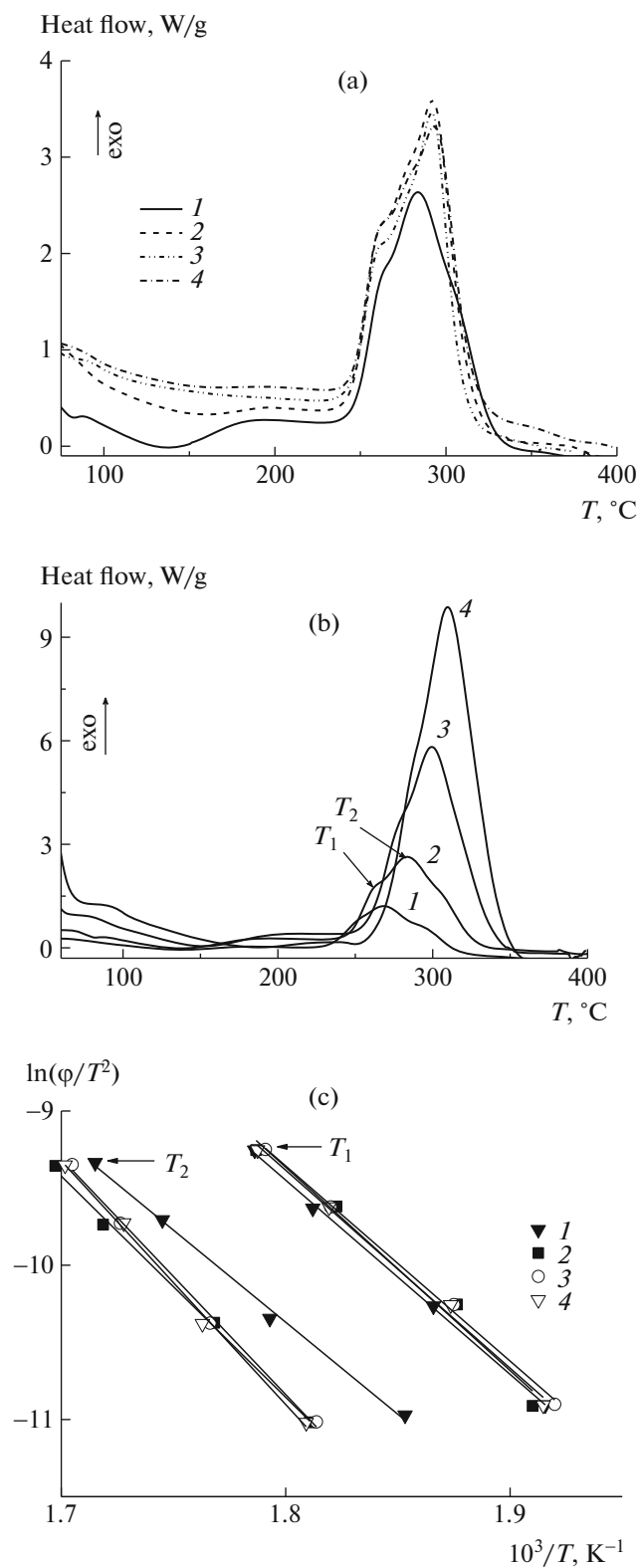


Fig. 9. Thermograms of terpolymers. (a) (1) T-MA, (2) T-BA, (3) T-EHA, and (4) T-LA measured in argon at a heating rate of 10°C/min; (b) T-MA measured in inert atmosphere at a heating rate of (1) 5, (2) 10, (3) 20, and (4) 30°C/min; and (c) results of treating thermograms of (1) T-MA, (2) T-BA, (3) T-EHA, and (4) T-LA samples in the coordinates of Eq. (1).

Table 4. Analysis of thermograms of the terpolymers shown in Fig. 9

Terpolymer	$T_g, ^\circ\text{C}$	$T_0, ^\circ\text{C}$	$T_1, ^\circ\text{C}$	$T_{\text{peak}}, ^\circ\text{C}$		$-\Delta H, \text{J/g}$	$-\Delta H/\Delta T$ (J/(g K))	E_a (cyclization), kJ/mol	
				1	2			ionic	radical
T-MA	111	233	338	263	285	740	7.0	107 ± 2	100 ± 4
T-BA	100	233	333	260	292	890	8.9	110 ± 10	119 ± 4
T-EHA	100	233	333	260	293	750	7.5	105 ± 4	127 ± 5
T-LA	93	236	333	260	294	800	8.2	107 ± 5	131 ± 5

T_0 and T_1 are the onset and end temperatures of the exothermic effect.

Table 5. Analysis of thermograms of films based on terpolymers AN-AA-alkyl acrylate synthesized under different regimes of introducing comonomers from the mixture containing 88.4 mol % AN, 1.8 mol % AA, and 9.8 mol % alkyl acrylate

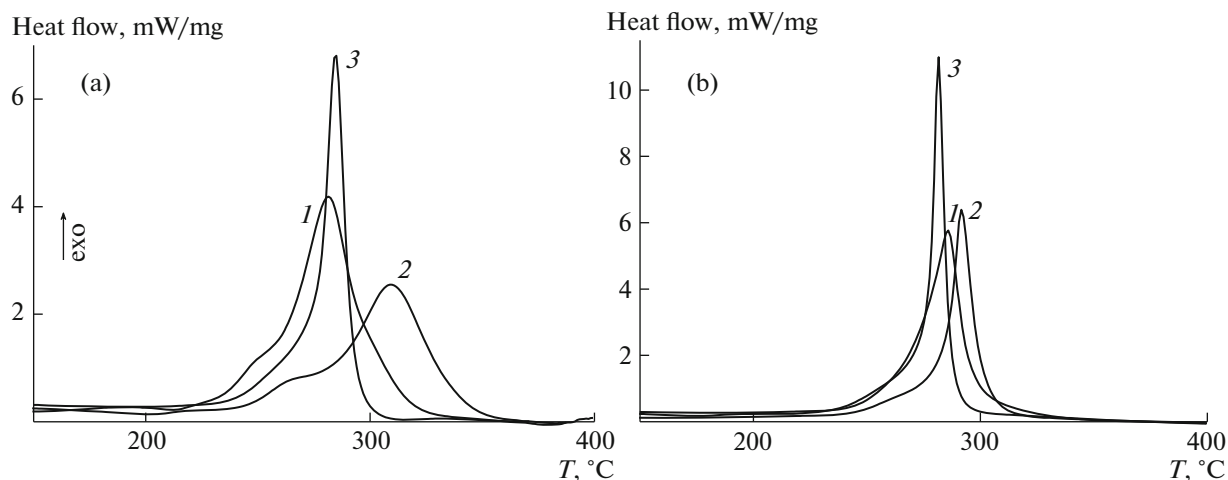
Monomer	Regime of introducing monomers	$T_0, ^\circ\text{C}$	$T_1, ^\circ\text{C}$	$T_{\text{peak}}, ^\circ\text{C}$		$-\Delta H, \text{J/g}$	$-\Delta H/\Delta T, \text{J/(g K)}$
				1	2		
MA	Instantaneous	212	343	252	281	875	6.5
	Continuous	226	336	260	286	777	7.1
BA	Instantaneous	221	364	265	309	738	5.2
	Continuous	226	329	262	292	610	5.9
LA	Instantaneous	224	311	256	285	625	7.2
	Continuous	227	307	251	282	656	8.2

intramolecular cyclization. The intensity of this band grows in the course of heat treatment.

In addition, new absorption bands at 3350 (ν_{NH}), 1376 ($\delta_{\text{C-H}}$, CH), 1246 and 1172 ($\nu_{\text{C-N}}$, $\nu_{\text{C-O}}$), and

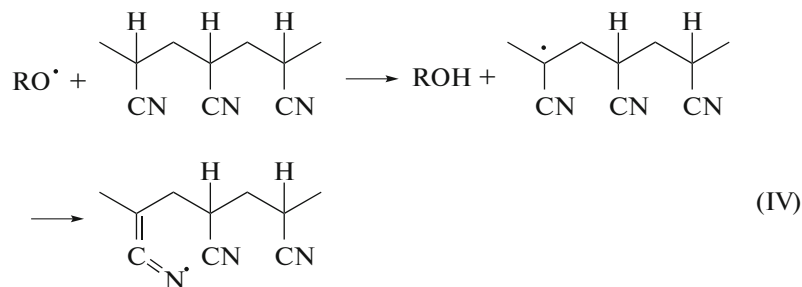
803 cm^{-1} ($\delta_{\text{C=C-H}}$) appear in the spectra which can be assigned to conjugated bonds formed in the system.

The absorption band at 1728 cm^{-1} corresponding to the carbonyl group $\nu_{\text{C=O}}$ shifts under heating to a long-

**Fig. 10.** Thermograms of terpolymers synthesized with (a) instantaneous and (b) continuous introduction of AA and alkyl acrylate (1) MA, (2) BA, and (3) LA into copolymerization. The thermograms were measured in the inert atmosphere at a heating rate of 10°C/min.

wave region and is observed as a shoulder at $\sim 1720\text{ cm}^{-1}$. Simultaneously, a new band appears at 1660 cm^{-1} as a shoulder of the band due to stretching vibrations of $-\text{C}=\text{N}-$ (1580 cm^{-1}). According to the published data, these bands are assigned to vibrations of the carbonyl group of naphthyridine and acridone rings. Their appearance is associated with initiation of the cyclization reaction by the carboxyl groups of AA and formation of the corresponding cyclic structures.

Appearance of the absorption band at 803 cm^{-1} which is related to the formation of multiple bonds $\text{C}=\text{C}$ is unexpected, because in the inert atmosphere at 250°C cyclization reactions are expected. Multiple bonds $\text{C}=\text{C}$ in PAN are usually formed in air through oxidation and dehydrogenation reactions [11]. It may be assumed that, along with reaction (IIIb), reaction (IV) also proceeds; as a result, bonds $\text{C}=\text{C}$ appear.



A comparative quantitative analysis of the rate of conversion of nitrile groups was performed using Eqs. (2) and (3) to calculate the fraction

of unreacted nitrile groups ϕ_{CN} and the degree of stabilization E_s during cyclization (Fig. 12).

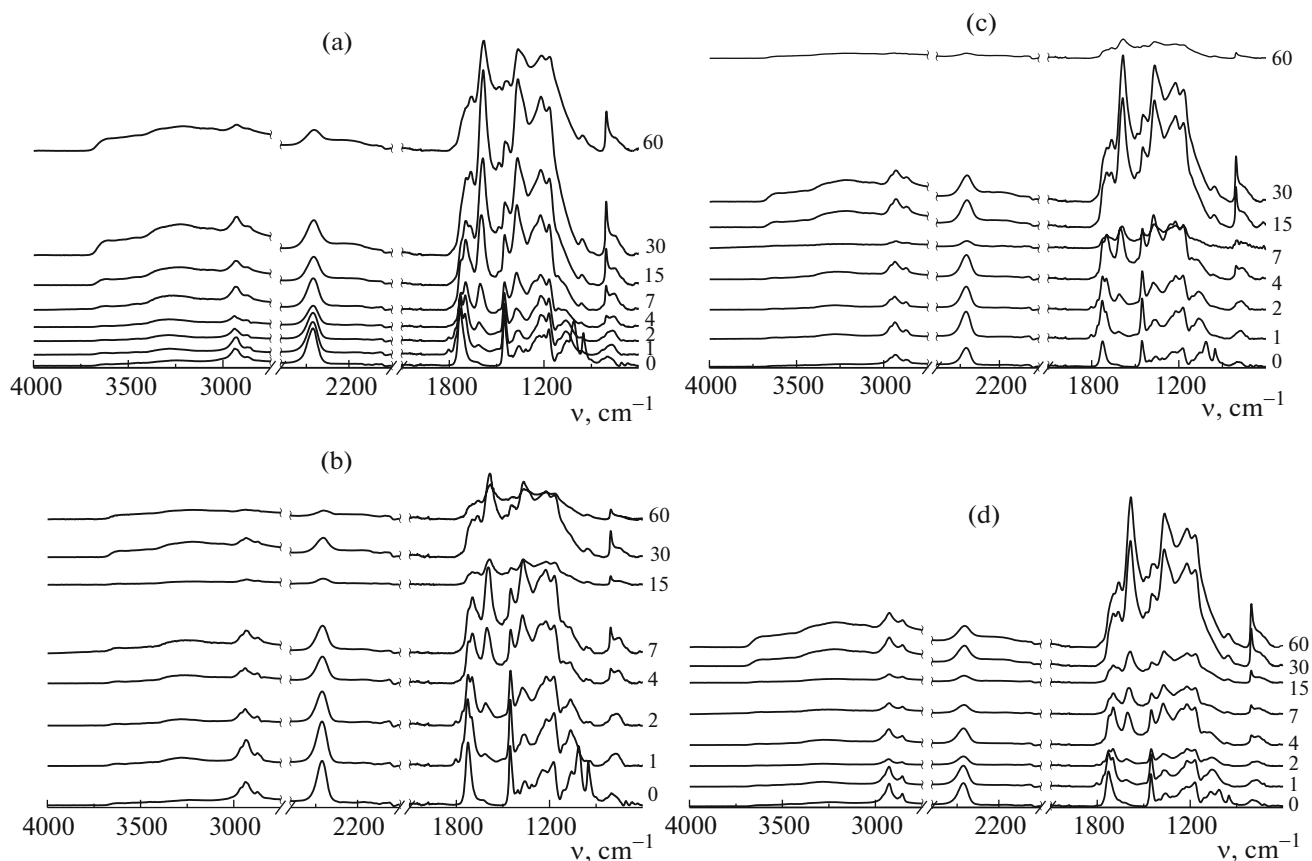


Fig. 11. IR spectra of (a) T-MA, (b) T-BA, (c) T-EHA, and (d) T-LA terpolymers measured after thermal treatment in inert atmosphere at 250°C for different time. Numerals at curves are the times of heat treatment in minutes.

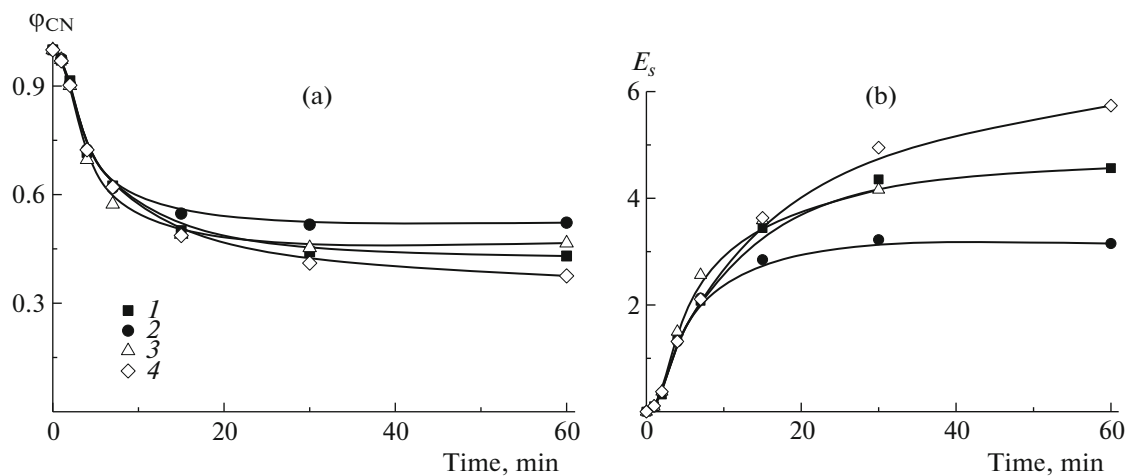


Fig. 12. Time dependence of (a) the amount of residual $-C\equiv N$ groups ϕ_{CN} and (b) the degree of stabilization E_s for terpolymers thermally treated in the inert atmosphere at 250°C.

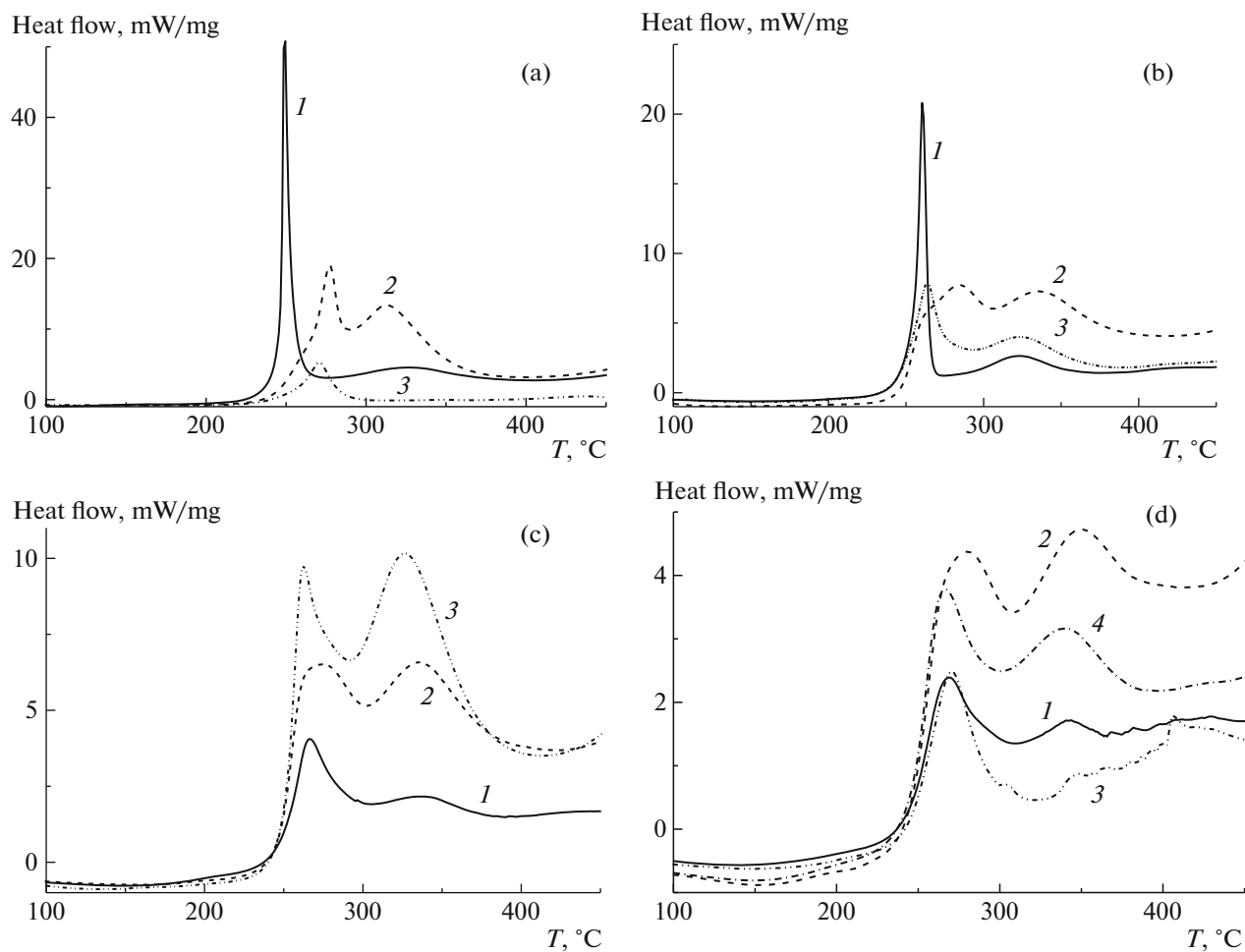


Fig. 13. Thermograms of copolymers AN-MA-AA measured in an atmosphere of air at a heating rate of 10°C/min. AN : AA = (a) 98 : 2, (b) 95 : 5, (c) 93 : 7, and (d) 90 : 10; AA : MA is (a) (1) 2 : 0, (2) 2 : 2, and (3) 2 : 1; (b) (1) 5.0, (2) 5 : 5, and (3) 5 : 1; (c) (1) 7 : 0, (2) 7 : 3.5, and (3) 7 : 1.4; and (d) (1) 10 : 0, (2) 10 : 5, (3) 10 : 2, and (4) 10 : 1.

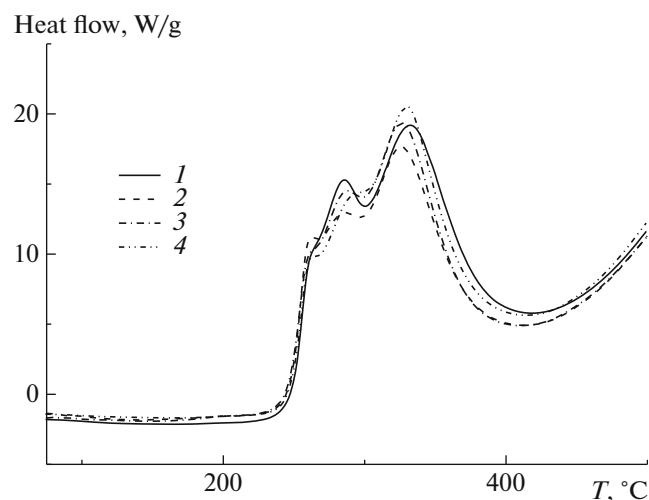


Fig. 14. Thermograms of terpolymers (1) T-MA, (2) T-BA, (3) T-EHA, and (4) T-LA measured in air at a heating rate of 10°C/min.

It is clear that, under isothermal conditions, cyclization develops fairly rapidly, during heating for the first 10 min; then its rate decreases; and already in

1 h, the fraction of unreacted groups is about 0.4 (Fig. 12a). A comparison with similar data reported for binary copolymers [25] shows that the rate of cyclization decreases in the sequence of copolymers (AN-AA)–(AN-AA-alkyl acrylate)–(AN-alkyl acrylate). The nature of alkyl acrylate in the terpolymers insignificantly influences the kinetics of the process, as opposed to the binary copolymers AN-alkyl acrylate [25]. This can apparently be explained by the fact that, at a given temperature, cyclization according to the ionic mechanism via AA units is the most probable. The degree of stabilization E_s enables one to evaluate development of the system of polyconjugated bonds. With an increase in the time of thermal treatment, E_s increases for all the tested samples and for T-LA assumes the maximum value. This distinguishes the terpolymers from the binary systems AN-alkyl acrylate which are characterized by a slowed down development of the ladder structure which is the most district for AN-LA copolymers.

Thus, the thermal behavior of the terpolymers can be tuned by changing the nature of alkyl acrylate and the molar fraction of copolymers. In terms of the complete formation of the system of conjugated bonds, the use of lauryl acrylate is of greatest interest.

Cyclization reactions in air. From the practical point of view, the process of thermo-oxidative stabilization occurring under heating in air and including cyclization, oxidation, and dehydrogenation reactions is more important. The combination of these reactions is accompanied by a more intense exo effect than cyclization in the inert atmosphere (Fig. 13). If the fraction of AA in the terpolymer is less than 5 mol %, then an increase in the content of MA entails a rise in the thermal effect of reaction; at a higher content of AA, the reverse situation is observed. In general, the larger the content of AA and MA units in the terpolymer, the lower the intensity of the heat flow. Similar trends in the behavior of terpolymer in the air atmosphere appear with increasing length of the alkyl sub-

Table 6. Analysis of thermograms of terpolymers AN-AA-alkyl acrylate of various composition

AN : AA : alkyl acrylate	Alkyl acrylate	$T_{\text{peak}}, ^\circ\text{C}$	$-\Delta H, \text{J/g}$
98 : 2 : 2	MA	276, 313	5833
	BA	277, 328	4280
	LA	259, 320	7759
98 : 2 : 1	MA	271	791
	BA	273, 309	6105
	LA	256, 281, 318	8154
95 : 5 : 5	MA	263, 285, 335	3684
	BA	262, 288, 336	2852
	LA	259, 292, 330	7752
95 : 5 : 1	MA	263, 323	2144
	BA	263, 322	1752
	LA	260, 309	7884
93 : 7 : 3.5	MA	274, 335	3441
	BA	261, 289, 336	4359
	LA	265, 338	4846
93 : 7 : 1.4	MA	263, 326	4696
	BA	261, 332	3452
	LA	266, 341	2827
90 : 10 : 5	MA	280, 349	1740
90 : 10 : 2	MA	271, 340	493
90 : 10 : 1	MA	267, 339	1504

Table 7. Analysis of thermograms of films based on terpolymers AN-AA-alkyl acrylate synthesized under various regimes of introducing comonomers from the mixture containing 88.4 mol % AN, 1.8 mol % AA, and 9.8 mol % alkyl acrylate

Monomer	Regime of introducing AA and alkyl acrylate	$T_{\text{peak}}, ^\circ\text{C}$			$-\Delta H, \text{J/g}$
		1	2	3	
MA	Instantaneous	285	366	—	807
	Continuous	264	293	336	1944
BA	Instantaneous	268	316	—	1262
	Continuous	266	290	—	946
LA	Instantaneous	260	281	324	5280
	Continuous	258	280	—	896

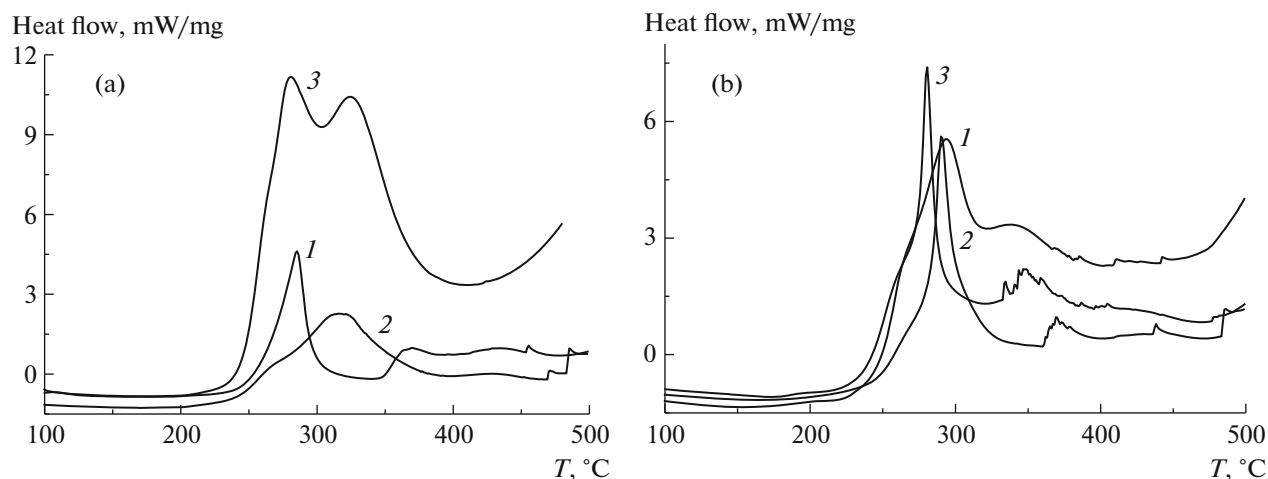
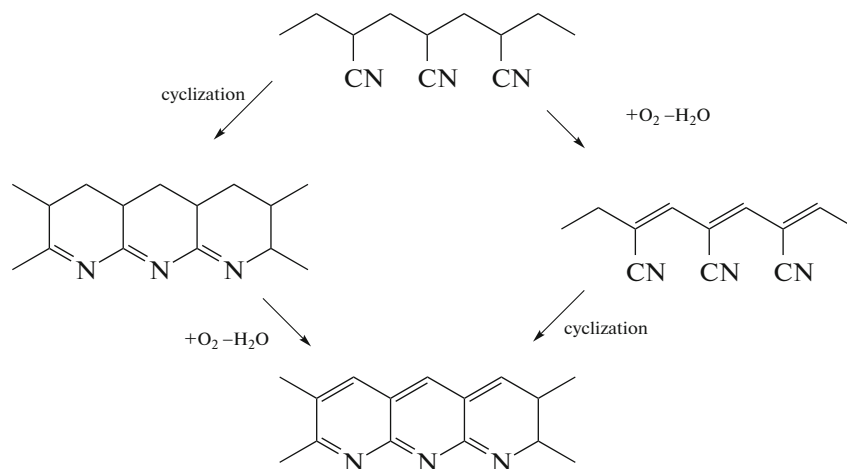


Fig. 15. Thermograms of the terpolymers synthesized with (a) instantaneous and (b) continuous introduction of AA and alkyl acrylate (1) MA, (2) BA, and (3) LA into copolymerization. The thermograms were measured in air at a heating rate of 10°C/min.

stituent in alkyl acrylate (Table 6). With lengthening of alkyl substituent in alkyl acrylate, the intensity of the low-temperature peak at AA : alkyl acrylate > 2 increases. Upon further increase in the content of alkyl acrylate, the intensity of this peak decreases abruptly and the difference in the thermal behavior of the terpolymers disappears (Fig. 14).

A change in chain microstructure should affect the thermal behavior of the terpolymers not only in an inert atmosphere but also an atmosphere of air. This is evident from comparison of the terpolymers synthesized from the same monomer mixture (88.4 mol % AN, 1.8 mol % AA, and 9.8 mol % alkyl acrylate) but under different regimes of introducing monomers: instantaneous or continuous (Fig. 15). In the former case, the thermal effect grows with lengthening of the alkyl substituent in alkyl acrylate; in the latter case, the thermal effect grows in the reverse order; the thermograms shift to low temperatures on going from MA to LA (Table 7).

Chemical processes occurring during heating of the terpolymers in air were investigated by IR spectroscopy. The films were heated at 225°C, since even under these conditions (DSC data) the exo effect was detected. A comparison of the IR spectra of terpolymer samples treated in the inert atmosphere (Fig. 11) and in air (Fig. 16) indicates that slight differences are observed in the range of 2850–2920 and 1720–1730 cm^{-1} for terpolymers containing MA, 2850–2920 and 1580–1730 cm^{-1} for terpolymers containing BA, and 1200–1730 cm^{-1} for terpolymers containing LA. These changes can be attributed to additional oxidation and dehydrogenation reactions proceeding in air. Note that the intensities of absorption bands which are related to the conversion of nitrile groups into imine ones change in the spectra earlier than the absorption band corresponding to the C=C group appears. Thus, it is conceivable that the cyclization reaction prevails over the dehydrogenation reaction and the pathway shown in the scheme on the right is implemented.



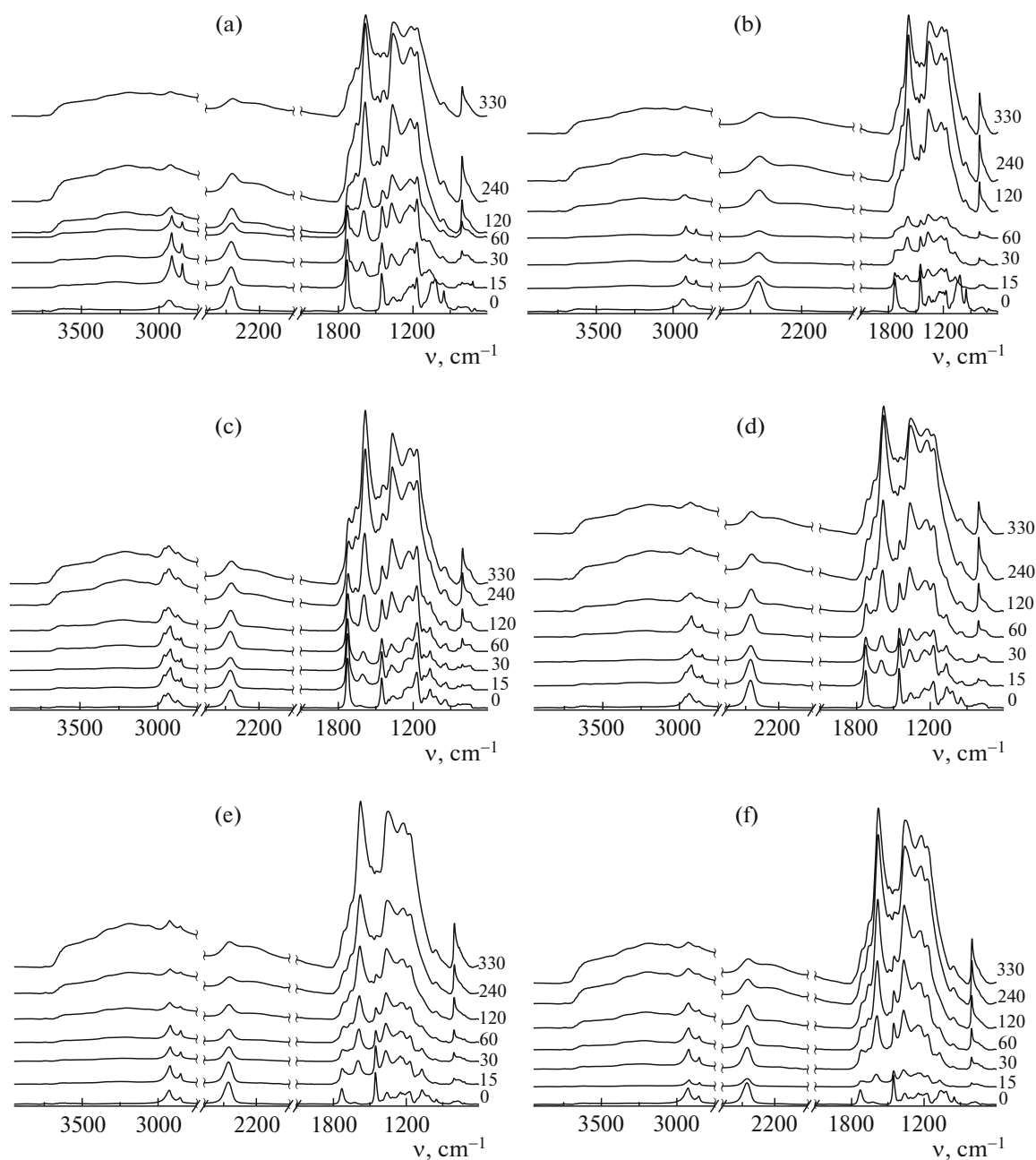


Fig. 16. IR spectra of terpolymers AN-AA-alkyl acrylate: (a, b) MA, (c, d) BA, and (e, f) LA synthesized with (a, c, e) instantaneous and (b, d, f) continuous introduction of AA and alkyl acrylate into the reaction mixture. The IR spectra were measured after heat treatment in air at 225°C for different time. Numerals at curves refer to the times of heat treatment in minutes.

As follows from comparison of the spectra of the terpolymers synthesized at the instantaneous and continuous introduction of AA and alkyl acrylate into the reaction mixture, qualitative changes in the spectra are independent of the chain microstructure. To quantify the changes, the fraction of unreacted nitrile groups ϕ_{CN} and the degree of stabilization E_s were calculated (Fig. 17). Depending on the nature of alkyl acrylate, the ratio between the rates of consumption of nitrile groups is different and depends on the procedure of

terpolymer synthesis. For example, for MA, the conversion of nitrile groups is higher at the instantaneous introduction of the monomers; for BA, the conversion of nitrile groups is independent of the synthetic procedure; and for AA and LA, the conversion is higher at their continuous introduction into the reaction medium (Fig. 17a). The degree of stabilization changes in a similar way and gradually increases with an increase in the length of the alkyl substituent. Thus, lengthening of the alkyl substituent in alkyl acrylate is

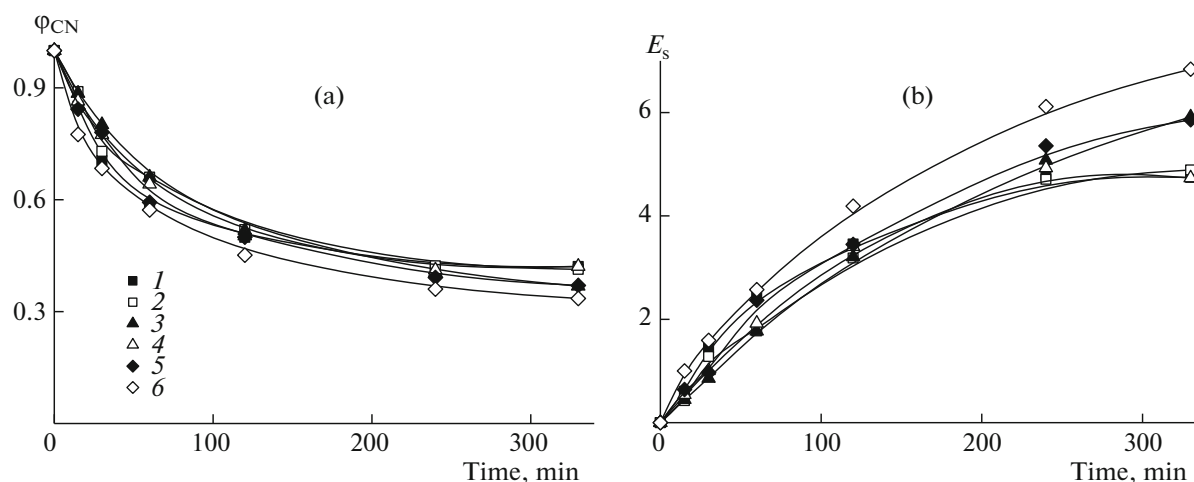


Fig. 17. Time dependence of (a) the degree of conversion of nitrile groups ϕ_{CN} and (b) the degree of stabilization E_s during heating in air at 225°C for films based on terpolymers AN-AA-alkyl acrylate (1, 2) MA, (3, 4) BA, and (5, 6) LA synthesized with (1, 3, 5) instantaneous and (2, 4, 6) continuous introduction of AA and alkyl acrylate into the reaction mixture.

favorable for an increase in the length of the system of conjugated bonds not only in an inert atmosphere but also in an atmosphere of air. It should be emphasized that the conversion of nitrile groups and the degree of stabilization are higher when the terpolymer is treated in air regardless of the ratio of acidic and ester groups in it (Figs. 12, 17).

CONCLUSIONS

The acrylonitrile terpolymers containing a monomer accelerating cyclization and an inert monomer, plasticizer, are of interest for the manufacture of carbon fibers. In this work, terpolymers containing AN, AA, and alkyl acrylate with different length of the alkyl substituent were first synthesized by RAFT polymerization. This made it possible to obtain a set of polymers having the desired MW and a narrow MWD but differing in the composition and unit distribution in a chain.

The heat treatment of the polymers in the inert atmosphere is accompanied by the cyclization reaction of nitrile groups. The contribution of ionic and radical mechanisms of its initiation depends not only on the content of AA in a terpolymer but also on the distribution of monomer units in a chain. The acrylate monomer has no effect on the rate of initiation of radical cyclization but can deteriorate development of the ladder structure because of its participation in the reaction of chain transfer. Therefore, upon the combined introduction of AA and alkyl acrylate units into PAN, the temperature interval of cyclization widens and the thermal effect of the reaction decreases. At almost the same content of AN in the terpolymer, widening of the temperature interval of cyclization and similar values of the thermal effect can be reached by

increasing the fraction of either AA or alkyl acrylate in the copolymer. We observed an unexpected phenomenon: the activation energy of radical cyclization increased with increasing length of the alkyl substituent in alkyl acrylate, which is not typical of binary copolymers AN-alkyl acrylates. In our opinion, the observed effect can be attributed to the different distribution of acrylate monomer units in a chain. This suggestion is confirmed in an independent experiment: a change in the chain microstructure at different regimes of introducing AA and alkyl acrylate into synthesis. Similar effects are observed in the thermal treatment of the terpolymers in air in which exothermic reactions of cyclization, oxidation, and dehydrogenation proceed.

Analysis of a change in the chemical structure of the terpolymers during thermal treatment in an inert atmosphere and air demonstrates that an increase in the length of the alkyl substituent in alkyl acrylate leads to a rise in the degree of stabilization, which takes the maximum value for the terpolymers containing lauryl acrylate.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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