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Homo- and Copolymers of Acrylonitrile: Effect of the Reaction Medium on the Thermal Behavior in an Inert Atmosphere

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Abstract—The effects of the synthesis conditions of acrylonitrile homo- and copolymers—such as the type of solvent, the homogeneity of the reaction medium, the type, and the amount of comonomer—on the conditions of formation and the structure of the polyconjugation system during pyrolysis of the synthesized polymers under an inert atmosphere are studied. In all experiments, the total concentration of the monomers, the concentration of initiator, the temperature of polymerization, and the conversion of the monomers remain constant.

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INTRODUCTION

In recent years, considerable attention of researchers has remained focused on polyconjugation systems as a variant of solid-state nanostructures with desired properties and controllable sizes. These systems include nanomaterials based on pyrolyzed PAN and its copolymers: carbon nanocrystalline materials [1]. Modern studies are directed not only at the development of new methods for the synthesis of these (co)polymers containing no less than 85 mol % acrylonitrile (the most promising amount for the targeted materials), which may be used to manufacture carbon fiber materials for various purposes [2–15], but also at the search for ways to control their physicochemical and physicomechanical properties. The thermal stability and chemical resistance of carbon-matrix-based materials, as well as their conductivity and mechanical properties, are responsible for their wide application areas: as fibers, as reinforcing fillers in the synthesis of polymeric composite materials, as carriers in the creation of nanocomposites possessing catalytic activity, in purification of various liquid and gaseous media, etc.

The PAN precursor is primarily prepared via radical polymerization, which is performed in a solution, an emulsion, or a suspension [16–22], depending on the further tasks. These variants of synthesis make it possible to vary in a wide range the molecular-mass characteristics of the polymers, the degree of crystallinity of PAN, the composition of macromolecules, and the distribution of monomer units in them and to introduce various end groups into macromolecules so that the desired system of conjugated bonds can be obtained.

Attempts were made to ascertain the relationship between the conditions of synthesis of PAN and AN-based copolymers and the characteristics of the products, their morphology, and their thermal behavior in both an inert and an air atmosphere [23–36]. In the first case, the reaction of intramolecular cyclization occurs; in the second case, reactions of cyclization, dehydration, and oxidation happen.

The only aim of the initial studies was to investigate the kinetics and mechanism of the cyclization of PAN [27, 37–39]. The results of these studies were often contradictory; therefore, it was inferred that the pyrolysis reactions of PAN samples of various prehistories are characterized by specific features (change in the temperature interval of reaction, the amount of evolved heat, and the type of low-molecular-mass products of pyrolysis), even though they have several features in common (exothermicity, occurrence in a relatively narrow temperature range, and loss in sample mass). The first attempt to systematize the data and to gain insight into the relationship between the conditions of synthesis of PAN and its thermal behavior was made in [25], in which the types of used organic solvents and initiators and the concentration of the monomer were varied and the resulting homopolymers were studied via DTA. It was found that the temperature of the exo-effect maximum, T_{peak}, depends on the reaction medium in which the PAN was synthesized: in water, this temperature was higher than that in an organic solvent; with an increase in the intrinsic viscosity of PAN estimated in DMF, the value of T_{peak} initially increases and then stops changing; for PAN formed via anionic polymerization, the value of T_{peak} is higher than that for PAN prepared via radical polymerization. In addition, the position of T_{peak} is affected by the level of branching of the polymer chain: the more pronounced this parameter, the lower the value of T_{peak} [26]. In [31, 32, 40], the pyrolysis of PAN was studied with the use of spectroscopic methods (IR, NMR, and mass spectroscopy), but unfortunately, generalization of these disembodied data was a problem.

The effects of various monomers; their amounts in copolymers; and, in some cases, chain microstructuring on the process of pyrolysis were studied in many papers devoted to the thermal behavior of acrylonitrile (AN)-based copolymers [27–35]. These comonomers may be divided into three groups: (i) comonomers accelerating cyclization (acrylic, methacrylic, and itaconic acids and acrylamide); (ii) comonomers inhibiting cyclization (styrene, its derivatives, vinylpyridines, and *N*-vinylpyrrolidone); and (iii) comonomers functioning as inert diluters, that is, not affecting the rate of pyrolysis (acrylates and methacrylates) [28–30]. However, no data are available on the influence of the conditions of synthesis (type of solvent, type of initiator, and temperature of polymerization) on the thermal cyclization of AN-based copolymers. The accessibility of modern precision scientific equipment and the use of synchronous thermal analysis and other combinations of physicochemical methods make it possible to study in detail the response of the analytical signal and to ascertain the relationship between the presence and types of residual solvents and comonomers, the partial hydrolysis of nitrile groups in the polymer, and the conditions of formation and the structure of the resulting polyconjugation system. Recently, a combination of DSC, diffuse-reflection IR spectroscopy, and IR pyrolysis was used to investigate the thermal behavior of AN homopolymers synthesized under conditions of homo- and heterophase polymerizations under the action of various kinds of initiation [41]. It was shown that during simultaneous variation of several factors, it is impossible to distinguish a single parameter controlling the rate of formation and the structure of the polyconjugation system (PCS). When molecular-mass characteristics are comparable, chain microstructure plays a noticeable role; when the molecular-mass distribution is broad, the effect of the chain microstructure diminishes. In addition, a considerable role is played by the specific interactions of PAN with a solvent, which facilitate the formation of conjugation with structural defects.

Similar defects may play an important role in the design, for example, of conducting materials. For example, quantum-chemical calculations [42] showed that monolayers of the pyrolyzed PAN may contain two kinds of defects: V_C- and V_N-defects. On the basis of their ratio, it is possible to control the conducting behavior of structurally modified composites. Therefore, they show promise for use in nanoelectronics: an increase in the amount of N atoms in the pyrolyzed PAN enhances the adsorption of atomic oxygen and shifts the conductivity of the adsorption complex toward the electronic side. In contrast, a decrease in the amount of nitrogen atoms in the pyrolyzed PAN may improve the efficiency of proton conductivity.

Thus, in accordance with the published data [25, 26], the prehistory of the sample—that is, the conditions of its synthesis, including the type of initiation, the mechanism of polymerization, and the homogeneity of the medium—have a strong effect not only on the exo-effect observed during the heating of PAN but also on the formation of the PCS.

It is evident that the correct comparison of the thermal behavior of polymers formed in various media requires that the number of varied parameters of synthesis should be minimized. With consideration for this fact and with the use of the approach described in [41], studies in this direction were continued.

The goal of this study is to examine effects of the type of solvent and type(s) of comonomer(s) on the characteristics of the resulting (co)polymers, their thermal behavior during cyclization in an inert atmosphere, and the structure of the polyconjugation system being formed.

EXPERIMENTAL

Homo- and copolymers of acrylonitrile were synthesized as described in [43]. Their characteristics are summarized in Table 1.

The molecular-mass characteristics of the polymers were studied via GPC on a GPC-120 chromatograph (PolymerLabs.) Analysis was performed at 50°C in DMF containing 0.1 wt % LiBr; the flow velocity was 1 mL/min. Two PLgel 5 μm MIXED B columns ($M = (5 \times 10^2)–(1 \times 10^7)$) were used for separation. The molecular masses were calculated relative to PMMA standards with the use of the Kuhn–Mark–Houwink coefficients known for PAN [44].

The IR spectra of the samples pelletized in a KBr matrix were measured on a Bruker IFS-66 v/s FTIR spectrometer in the range 4000–400 cm^{-1}. ATR IR spectra (Ge crystal) of the samples were recorded on a Hyperion 2000 IR microscope combined with a Bruker vacuum IFS 66 v/s spectrometer in the range 4000–600 cm^{-1}. The IR spectra were treated with the program OPUS (Bruker).

The compositions of the copolymers were quantitatively determined with the use of the following analytical bands in the IR spectra of every homopolymer: absorption bands due to the stretching vibrations of CN groups ($\nu_{CN} = 2244$ cm^{-1}) for AN, C=O bonds in the ester group ($\nu_{C=O} = 1735$ cm^{-1}) for methyl acrylate (MA), and a broad band with a maximum at 1710 cm^{-1}

Table 1. Conditions of synthesis and characteristics of the polymers isolated at limiting conversions of monomers

Solvent	[AIBN], mol/L	Total concentration of comonomers, mol/L	Composition of the comonomer mixture, mol %			Composition of copolymer, mol %			$M_w \times 10^{-3}$	M_w/M_n
			AN	MA	ITA	AN	MA	ITA		
DMSO	0.8×10^{-2}	4.7	100	–	–	100	–	–	110	1.60
			96.9	3.1	–	96.2	3.8	–	85	1.97
			96.4	3.2	0.4	94.0	4.5	1.5	78	1.84
DMF	0.5×10^{-2}	4.9	100	–	–	100	–	–	42	1.65
			98.1	1.9	–	97.0	3.0	–	40	2.04
			96.9	3.1	–	96.0	4.0	–	40	1.99
			95.6	4.4	–	94.6	5.4	–	40	1.89
			97.3	2.3	0.4	95.7	3.3	1.0	41	1.81
			96.4	3.2	0.4	94.3	4.4	1.3	40	1.92
			95.1	4.5	0.4	92.7	5.6	1.7	41	1.90
Water	1.8×10^{-2}	2.7	100	–	–	100	–	–	207	3.00
			96.9	3.1	–	95.0	5.0	–	214	4.72
			96.4	3.2	0.4	93.8	4.8	1.4	255	2.84
NaNCS	1.3×10^{-2}	4.1	100	–	–	100	–	–	193	1.86
			96.9	3.1	–	95.7	4.3	–	168	1.85
			96.4	3.2	0.4	93.3	4.3	2.4	88	2.43
$ZnCl_2^*$	0.9×10^{-2}	2.9	100	–	–	94.6	Amide: 2.7	2.7	72	1.76
			96.9	3.1	–	92.6	4.3; Amide: 1.5	1.6	80	1.76
			96.4	3.2	0.4	94.1	3.1; Amide: 1.3	1.5	61	1.63

ITA is itaconic acid.

* For the composition of a copolymer synthesized in a solution of zinc chloride, the ITA column shows the total amount of acidic groups; the MA column additionally shows the amount of amide groups (amide) formed via hydrolysis during the synthesis of the polymers.

($\nu_{C=O}$ for group –C(O)OH) in itaconic acid. For every analytical band, molar-absorption coefficients ε were determined for solutions of homopolymers of various concentrations; for itaconic acid, the value of ε estimated for malonic acid was used. The compositions of the copolymers were calculated as described in [45]. The concentrations of components were determined with an error of 1%.

Heat effects observed during polymer heating were studied on a NETZSCH DSC 204F1 Phoenix differential scanning calorimeter (Germany) in an atmosphere of dried gas (air, argon) at a flow velocity of 100 mL/min in the range 30–500°C; the heating rate was 10 K/min. Measurements were performed with (co)polymer samples weighing 4–8 mg. The test sample was placed in a standard aluminum crucible without any cover. The results were treated with the help of the program NETZSCH Proteus® Software.

The IR pyrolysis of dry PAN powders was conducted for 15 min in a special laboratory pulsed-photon annealing device in an atmosphere of argon in the step-by-step mode at 100, 140, 160, 180, and 200°C [45]. The light sources were KG-220 halogen lamps, for which the radiation maximum was at 0.9–1.2 μm. The samples were poured into aluminum crucibles, which were then placed in a graphite cassette, which was an absolutely black body, and were adjusted on special quartz holders in a cylindrical quartz reactor containing 15 lamps on the external surface. The intensity of IR radiation was monitored from the heating temperature of the sample measured with a thermocouple. The temperature regulation was precise to within 0.25°C. After each step of annealing, ATR IR spectra were recorded.

RESULTS AND DISCUSSION

Effects of Reaction Media on the Compositions and Structures of Acrylonitrile (Co)Polymers

As was shown in [41], radical polymerization AN, regardless of the type of solvent selected for synthesis, yields atactic polymers with close amounts of heterotactic triads (~50%) [41]. It is important that the presence of a complexing agent in the reaction system (e.g., NaNCS) has no effect on the configurational composition of macromolecules, although these compounds influence the kinetics of the process via participation in the elementary event of chain growth [47].

Let us analyze the IR spectra of the homo- and copolymers.

The IR spectra of homopolymer samples (Fig. 1a) show all bands typical for PAN: stretching vibrations of CH groups are observed in the range of 2900–2860 cm^{-1}, and stretching vibrations of nitrile groups ν_{CN} are observed at 2244 cm^{-1}, respectively; bending vibrations δ_{CHH} are seen at ~1450 and 1360 cm^{-1}; mixed δ_{CHH} and rocking γ_{CH_2} vibrations are observed

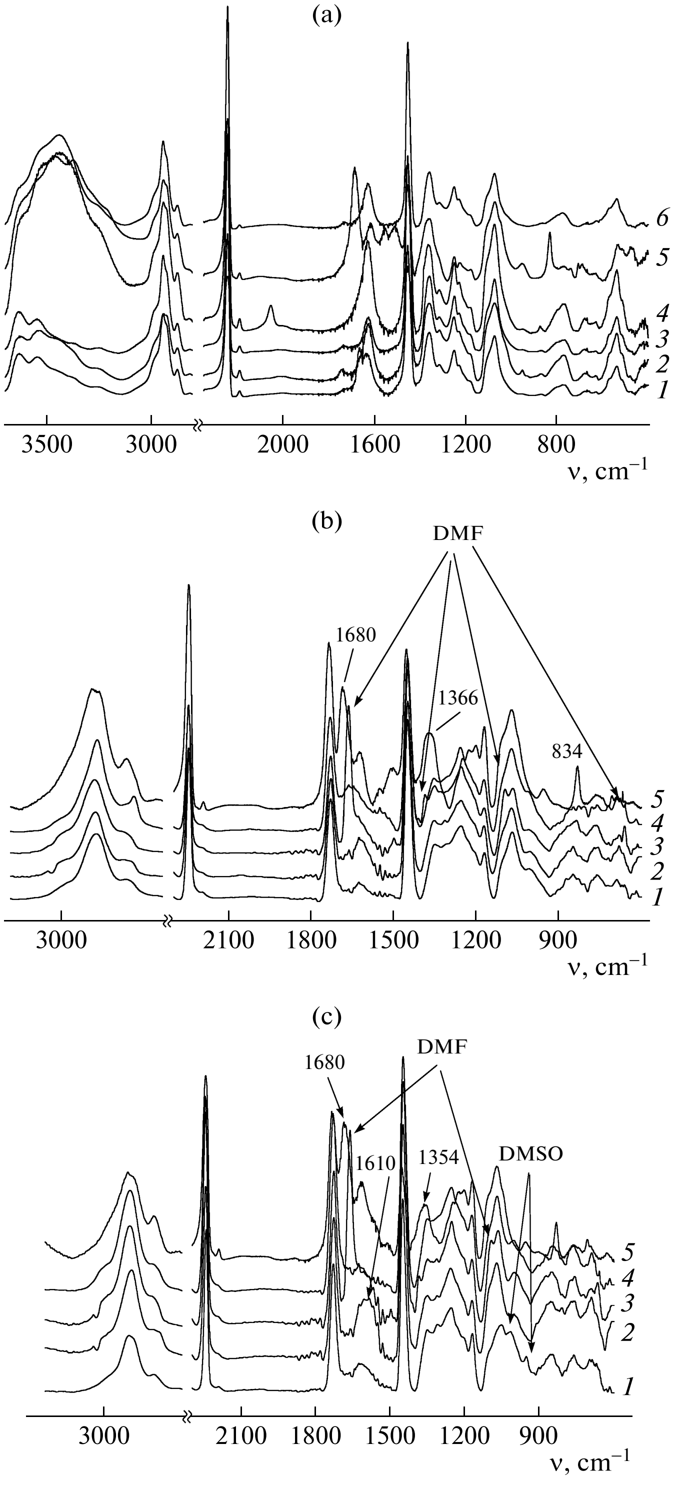


Fig. 1. (a) IR absorption spectra of PAN samples and (b, c) ATR IR spectra of (b) initial binary and (c) ternary AN copolymers synthesized in various media: (a) (*1*) DMF, (*2*) DMSO, (*3*) H_2O, (*4*) the NaNSC solution, and (*5*) the $ZnCl_2$ solution; (*6*) the IR spectrum of the PAN homopolymer (Aldrich) is given for comparison; (b, c) (*1*) DMSO, (*2*) a NaNSC solution, (*3*) DMF, (*4*) water, and (*5*) a $ZnCl_2$ solution.

at ~1073 cm^{-1}; and weak absorption bands are seen at 1250 and 762 cm^{-1} [48]. The spectrum of the sample synthesized in DMF (curve *1*) exhibits the absorption band due to the stretching vibrations of C=O groups (1667 cm^{-1}) of the residual solvent; all spectra of the homopolymers show the absorption bands of water (1620 and ~3400 cm^{-1}) sorbed during preparation of the pellets in the KBr matrix. In the ATR IR spectrum of the initial PAN formed in the aqueous solution of sodium thiocyanate, absorption bands corresponding to thiocyanate groups (2071, 1022, and 957 cm^{-1}, curve *4*) make themselves evident.

The position of the absorption band related to the stretching vibrations of nitrile groups does not change with variation in the polymerization medium; in contrast, the band at 1450 cm^{-1} (δ_{CHH}) is sensitive to a change in the conformational composition of the elementary unit: for samples synthesized in organic solvents and salt solutions, its contour is split into several maxima.

In addition, note that the IR spectrum of PAN synthesized in a solution of $ZnCl_2$ exhibits low-intensity absorption bands due to amide and associated acidic groups (at 1687, 1550, 1514, 830, and 469 cm^{-1}). It may be suggested that the appearance of these bands is associated with the partial hydrolysis of nitrile groups; it is quite possible that this reaction occurs at elevated temperatures in acidic media [49].

An analysis of the IR spectra of AN–MA binary copolymers (Fig. 1b) prepared in various media indicates that, for all of the copolymers, the maximum of the absorption band due to the stretching vibrations of nitrile groups ($\nu_{C\equiv N}$) shifts toward the longwave region relative to its position for the homopolymer. Note that for the copolymers formed in solutions of NaNCS and $ZnCl_2$, DMF, and water, this shift is insignificant, while for the copolymer prepared in DMSO, this shift amounts to 2.5 cm^{-1}. With consideration for the fact that the stretching vibrations of nitrile groups are slightly sensitive to a change in the environment and the related change in polarization, this effect is substantial.

As was shown in [50], transition-metal salts affect splitting of the absorption band corresponding to the stretching vibrations of CN bonds and shifts of the maxima toward the longwave region and shortwave region of the spectrum that are due to formation of donor–acceptor complexes. In accordance with [51], the above-described shift in the maximum of the absorption band toward the longwave region provides evidence for coordination via π electrons of the triple bond C≡N; as a consequence, redistribution of the electron density on the bond occurs and it deviates from an angle of 180°C. It is reasonable to assume that this change in geometry will influence the formation of conjugated structures during IR pyrolysis.

A similar effect was observed for the absorption band corresponding to the stretching vibrations ($\nu_{C=O}$, 1730 cm^{-1}); however, in this case, the maximum shift (3 cm^{-1}) is typical for the sample synthesized in a solution of sodium thiocyanate. In contrast, in the case of the absorption band related to the bending vibrations of CH_2 groups (δ_{CHH} 1450 cm^{-1}), the position of the maximum changes insignificantly. Low-intensity absorption bands of the residual solvent are observed in the IR spectra of the binary copolymers synthesized in DMF (1668, 1501, 1388, 1095, and 660 cm^{-1}) and water (bending vibrations δ_{H-O-H}, 1640 cm^{-1}).

It is important that the IR spectra of the copolymers synthesized in a solution of $ZnCl_2$ and via precipitation polymerization show absorption bands due to the products of hydrolysis: at 1680, 1366, 834 cm^{-1}, etc. In addition, the facts that the maximum of absorption band δ_{CHH} shifts by 5 cm^{-1} relative to its position in the spectrum of the homopolymer and that the ratio of intensities of the absorption bands at 1300–1150 cm^{-1} changes suggest that there are chemical and conformational differences in the macromolecules of the homopolymer and the copolymer of acrylonitrile. A similar shift in the maximum of the absorption band corresponding to the bending vibrations of CH_2 groups was explained by noncovalent interactions of functional groups in the polymer backbone [52].

The IR spectra of the ternary copolymers are more complicated (Fig. 1c); the presence of the carboxyl group in a macromolecule may manifest itself in the IR spectrum in a different manner, depending on the environment. For example, the dimers of carboxylic acids with inner hydrogen bonds are characterized by absorption bands at 1670–1650 cm^{-1}, while the COO^- ion with delocalized electron density is characterized by two absorption bands at 1610–1550 and 1420–1300 cm^{-1}. The C=O group in the aromatic carboxylic acid absorbs at 1680 cm^{-1}, and the chelate structure of the enol form makes itself evident as absorption bands at 1656 and 1618 cm^{-1}, with the first band corresponding to the bound carbonyl (the chelate bond) and the second band corresponding to the double bond C=C [48]. Hence, any conjugation entails a reduction in the frequency of vibrations of C=O bonds.

In the IR spectra of the terpolymers formed in DMSO, DMF, and an aqueous solution of sodium thiocyanate, absorption bands were observed at 1610 cm^{-1}, while for the copolymer synthesized via precipitation polymerization in water, another low-intensity absorption band was seen at 1695 cm^{-1}. It may be supposed that, along with the formation of acidic and/or ionic groups during the partial hydrolysis of MA ester groups, small additions of itaconic acid in the synthesis of the terpolymer facilitate the formation of pseudocyclic structures in the copolymer; as a result, redistribution (delocalization) of electron density of the C=O bond occurs and, accordingly, it shifts toward the longwave region of the IR spectrum. The IR spectrum of the terpolymer synthesized in an aqueous solution of $ZnCl_2$, like the IR spectra of the

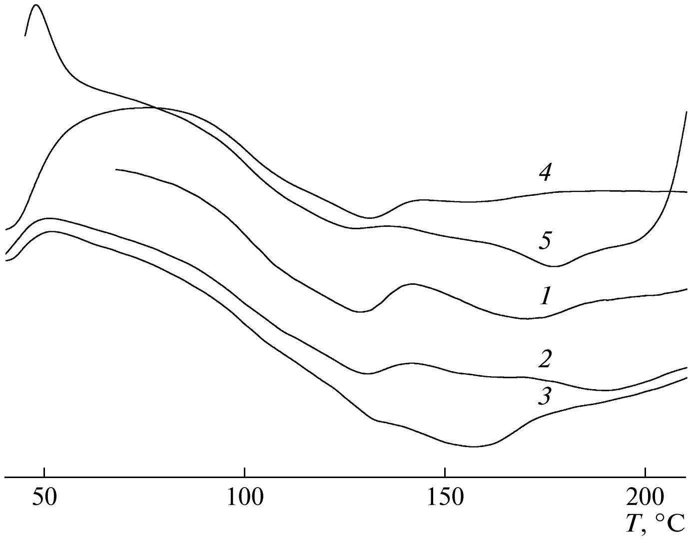


Fig. 2. Fragmented DSC curves of homopolymers of AN synthesized in various solvents: (*1*) DMSO, (*2*) DMF, (*3*) water, (*4*) an aqueous solution of NaNCS, and (*5*) an aqueous solution of $ZnCl_2$.

homopolymer and the binary copolymer, shows additional intense absorption bands assigned to the products of hydrolysis: the band is split into two maxima at 1737 and 1731 cm^{-1}, and absorption bands appear at 1680, 1618, 1354, and 832 cm^{-1}.

The position of the maximum of the absorption band due to the stretching vibrations of nitrile groups in the terpolymers, as opposed to that in the case of the binary copolymers, is almost the same as the corresponding position in the case of the homopolymer, and the ratio of absorption bands in the region of mixed stretching and bending vibrations of C–O groups changes slightly in all the terpolymers except that synthesized in a solution of zinc chloride.

In the IR spectra of the terpolymers, low-intensity absorption bands related to the residual solvent (DMF, H_2O, or DMSO) are observed at 1052 and 952 cm^{-1}. Note that the absorption bands typical for NaNCS are not found in the IR spectra.

Moreover, the type of reaction medium affects the compositions of the samples (Table 1). The molar fraction of MA in the binary copolymers successively decreases in the following sequence of solvents: DMSO, DMF, a solution of sodium thiocyanate, water, and a solution of zinc chloride. The degree of hydrolysis in these samples changes in the same sequence. The terpolymers prepared in DMSO or DMF are characterized by close compositions, while the polymers formed in water and in an aqueous solution of salts are enriched with MA and itaconic acid, respectively.

Different conformations of macromolecules, changes in the compositions of the copolymers, and the presence of residual solvent may affect the thermal behavior of the copolymers, that is, the reactions of cyclization and thermo-oxidative stabilization.

Phase State of Polymers

The literature data available on the phase state of PAN are extremely contradictory. In accordance with [29], there are two glass-transition temperatures: the first temperature, $T_{g,1}$, is in the temperature range near 70–75°C, while the second temperature, $T_{g,2}$, which is determined by the dipolar interaction of nitrile groups, is 130–140°C [29]. In [36], either a single glass-transition temperature of ~100–105°C or two glass-transition temperatures at $T_{g,1} \sim 100$°C and $T_{g,2} \sim 150$°C were described [36]. In this case, the degree of crystallinity of PAN is 40–50%, as evidenced by X-ray diffraction.

For the above-described homopolymers, a change in the heat capacity of a sample and a drift in the baseline in the range 70–200°C on the DSC curves may be explained by the presence of two glass-transition temperatures (Fig. 2). For PAN synthesized in DMSO (curve *1*) and DMF (curve *2*), $T_{g,1} \sim 100$°C and $T_{g,2} \sim 150$°C; for PAN synthesized in water (curve *3*), $T_{g,1} \sim 100$°C and $T_{g,2} \sim 140$°C; for PAN synthesized in the aqueous solution of zinc chloride (curve *4*), $T_{g,1} \sim 100$°C and $T_{g,2} \sim 160$°C; and for PAN synthesized in the aqueous solution of sodium thiocyanate (curve *5*), $T_{g,1} \sim 100$°C solely. Note that the low-temperature transition is very blurred and that the value of $T_{g,1}$ is conditional.

The copolymers feature a single glass-transition temperature; the temperature interval of change in the heat capacities of the samples isolated from homogeneous reaction mixtures is narrower (15–20°C). As is seen from Table 2, the incorporation of MA and itaconic acid into the polymer chain has practically no effect on the values of $T_{g,1}$ for the samples prepared in DMSO and DMF. For the copolymers formed via precipitation polymerization in water, the temperature

Table 2. DSC data obtained for polymers during their heating under an inert atmosphere

Medium	System	T_g	T_{ans}	T_{end}	T_{peak}	ΔH, J/g
DMSO	AN	~100, ~150	239.3	307.0	269.3	1665
	AN–MA	101	245.8	318.0	298.4	1402
	AN–MA–ITA	101	180.7	323.0	286.8	1781
DMF	AN	~100, ~150	234.0	310.2	272.8	1599
	AN–MA	101	238.0	316.3	292.0	1587
		100	244.9	318.9	298.2	1423
		99	245.0	324.0	300.2	1329
	AN–MA–ITA	101	216.9	338.4	287.4	1497
		98	205.0	352.7	291.3	1948
		101	204.1	356.1	288.9	1763
Water	AN	~100, ~140	232.2	301.6	269.5	1645
	AN–MA	101	231.5	318.2	297.0	1911
	AN–MA–ITA	101	217.0	321.7	291.6	1811
NaNCS	AN	~100	263.8	311.7	286.7	1583
	AN–MA	101	266.5	322.9	301.4	1530
	AN–MA–ITA	105	254.7	321.5	300.5	1406
$ZnCl_2$	AN	~100, ~160	200.9	305.3	226.8, 259.6	1106
	AN–MA	102	217.4	366.7	284.7	1471
	AN–MA–ITA	108	213.4	374.9	260.2, 284.6	1421

dependences of heat capacity shows a broad blurred devitrification interval, a circumstance that may indicate their high compositional heterogeneity, but the values of $T_{g,1}$ are the same as that for the homopolymer. The glass-transition temperatures of the AN–MA binary copolymers formed via complex-radical polymerization are likewise equal to the $T_{g,1}$ values of homopolymers, but after the addition of itaconic acid, the $T_{g,1}$ values increase.

Thermal Behavior of Copolymers in an Inert Atmosphere

Heating of PAN at temperatures above 200°C under an inert atmosphere is accompanied by intra- and/or intermolecular cyclization reactions yielding the PCS; this reaction is accompanied by a marked release of heat and a significant loss in mass of a sample [23]. The rate of this reaction and the structure of the PCS are affected by several factors: the conditions of synthesis, which determine the structure and length of polymer chains; the method of sample isolation (the presence of residual solvent, a monomer, and an initiator); morphology (powder, film, or fiber); the content of the monomer; the type of monomer; etc. [25, 26]. Even though dozens of studies have been devoted to the pyrolysis of homo- and copolymers of AN in an inert atmosphere, there is no clear correlation between the effect of the above-mentioned factors, the temperature interval of the exo-effect corresponding to cyclization and its value, and the structure of the PCS. In what follows, the effects of the conditions of synthesis and the compositions of polymers on the thermal behavior of PAN samples will be considered consecutively.

DSC study of the thermal behavior of the polymers. As was found in [41], the type of solvent used in the synthesis may alter the thermal behavior of PAN, thereby causing a noticeable shift in the onset temperature of the cyclization reaction [41]; however, the experimental conditions of preparing these samples (type of initiator, concentration of reagents, and temperature) were appreciably different. In this study, the conditions of synthesis for all polymers were selected to be maximally similar (Table 1); as a result, the amount of variable parameters was reduced to the minimum.

Figure 3a plots the DSC curves of the AN-based homopolymers formed in various media. The DSC curves (curves *1–3*) obtained for PAN samples prepared in organic solvents and water show a single narrow exothermal peak in a close temperature interval; the temperatures of its maximum differ by no more than 3°C, and the intensities of heat release differ by 10–15% (Table 2). Note that these polymers have different molecular masses and widths of the molecular-mass distributions. In contrast, the thermal behaviors of PAN samples synthesized in the concentrated aqueous solutions of sodium thiocyanate and zinc chloride, that is, via complex-radical polymerization, differ appreciably. In the first case, the cyclization reaction is observed at higher temperatures, but occurs in the narrow temperature range (curve *4*). In the second case, the onset temperature of cyclization decreases abruptly (>50°C) and the DSC curve becomes polymodal with two defined peaks of different intensities (curve *5*). This evidence testifies that the thermal behavior of PAN is independent of its molecular-mass distribution; note also that the end-groups of macromolecules of the mentioned samples are the same and their stereoregularities are almost the same. In this case, the presence of a certain amount of hydrolyzed nitrile groups (amide and carboxyl) in the polymer causes a sharp reduction in the onset temperature of cyclization, while the presence of residual thiocyanate entails an increase in this value.

The incorporation of the comonomer into the polymer chain may lead to different effects. In accordance to the published data, the effect of MA on the thermal cyclization of PAN is reduced to deterioration of chain regularity; as a result, this reaction occurs at higher temperatures [28]. In contrast, itaconic acid (or any other carboxylic acid) shifts the onset of cyclization toward low temperatures [31].

It may be assumed that, in the case of the AN–MA binary copolymers synthesized in various media, the relationships are the same as those for the homopolymers. In fact, as is clear from Fig. 3b, the maximum temperatures of the exo-effect for the copolymers prepared in DMSO, DMF, and water are close (curves *1*–*3*). In this case, cyclization of the polymer formed via precipitation polymerization begins earlier and the heat release is more intense than that in the case of the copolymers isolated from organic solvents. Remember that IR studies registered trace amounts of residual solvents—DMF and water—and the products of hydrolysis.

An increase in the amount of MA in the copolymer formed in DMF brings about a shift in the exo-effect and its maximum to the high-temperature region and a decrease in the intensity of heat release (Table 2). A comparison of the above results with the published data obtained for samples of various compositions that were synthesized via polymerization in water [28] reveals that the heterogeneous character of the process is responsible for other relationships. At a greater fraction of MA in the copolymer, the cyclization begins earlier, but the maximum temperature of the exo-effect increases. These differences probably are related to a higher compositional heterogeneity of macromolecules formed via precipitation polymerization rather than to the presence of residual solvent and the partial ionization of hydrolyzed ester groups.

The character of the thermal behavior of the copolymers synthesized via complex-radical polymerization is close to that of the corresponding homopolymers. In the case of sodium thiocyanate (Fig. 3b, curve *4*), the cyclization reaction occurs at higher temperatures than those in the case of DMSO, DMF, or water; in the case of zinc chloride, in contrast, the cyclization reaction occurs at low temperatures and in a wide temperature range (Fig. 3b, curve *5*; Table 2).

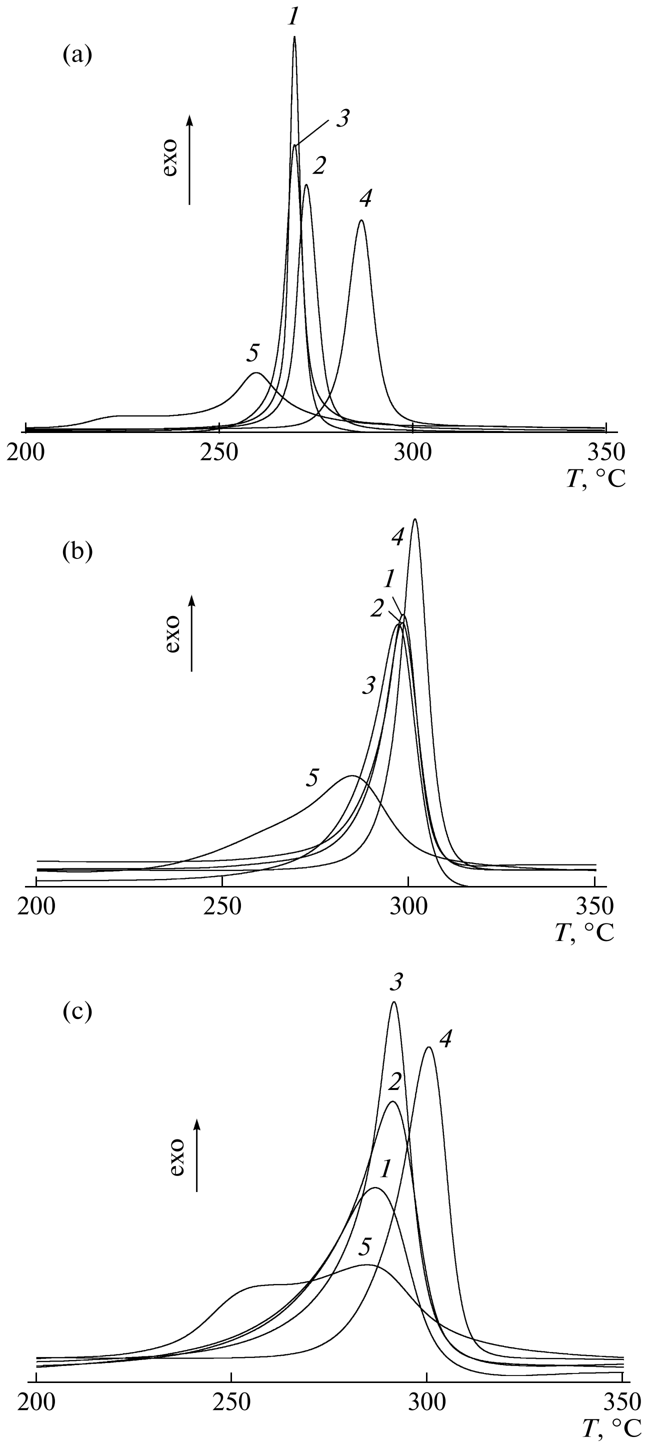


Fig. 3. DSC curves measured in an inert atmosphere for (a) AN homopolymers, (b) AN–MA copolymers, and (c) AN–MA–itaconic acid copolymers prepared in (*1*) DMSO, (*2*) DMF, (*3*) water, and (*4*, *5*) water–salt solutions of (*4*) NaNCS, and (*5*) $ZnCl_2$.

In comparison to homopolymers, binary copolymers formed under similar conditions feature thermal cyclization that begins and ceases at higher temperatures; a wider temperature interval of the exo-effect; and, except in the case of the precipitation polymerization and the process with the participation of $ZnCl_2$, a decrease in the intensity of heat release.

The additional incorporation of itaconic acid into a macromolecule, as is known, causes a shift in the onset of cyclization toward low temperatures [29–31]. It was found that, in this case, the observed effects are substantially influenced by the conditions of synthesis, which in turn determine the forms of itaconic acid in the polymer: ionized, nonionized, bound to the anhydride cycle, etc.

Figure 3c shows the DSC curves of the terpolymers formed in various solvents. The copolymers prepared in organic solvents are characterized by a broad temperature interval of the exo-effect; for the sample synthesized in DMSO (curve *1*), the onset and end of the exo-effect are shifted toward low temperatures by 20–25°C relative to those in DMF (curve *2*) and the intensity of the exo-effect is lower, while the position of the maximum remains practically the same. As is evident from comparison with the DSC curves of the binary copolymers, the onset of the cyclization reaction for terpolymers is ~40–50°C lower. An increase in the concentration of MA at a fixed concentration of itaconic acid in the initial mixture AN–MA–itaconic acid polymerized in DMF leads to widening of the temperature interval of the exo-effect due to a decrease in its onset temperature and an increase in its end temperature; in this case, the maximum temperature of the exo-effect varies within 2–4°C. In the case of binary copolymers, other regularities are valid (see above).

During cyclization of the terpolymer synthesized via precipitation polymerization (curve *3*), heat release begins ~15°C lower than that of the AN–MA copolymer but at higher temperatures than those for the terpolymers prepared in organic media.

The use of sodium thiocyanate made it possible to decrease the onset temperature of the exo-effect by ~8°C (curve *4*); however, the position of its maximum and its intensity are almost the same as those of the AN–MA binary copolymer. Among all studied terpolymers, precisely in this case the exo-effect is observed at the highest temperature. The DSC curve of the terpolymer synthesized in the solution of zinc chloride is polymodal; the temperatures corresponding to the onset and end of the exo-effect for binary and ternary copolymers are similar; however, the ratio of peak intensities changes (curve *5*).

Thus the thermal behavior of homo- and copolymers prepared via a complex-radical polymerization differs strongly from other samples, and the effect of the solvents used in synthesis is the most pronounced in the case of terpolymers.

Study of the thermal behavior of polymers via IR pyrolysis and ATR IR spectroscopy. The formation of PCS during IR pyrolysis obeys the same mechanism as that of the thermal transformations of PAN; however, the time of reaction shortens abruptly [46]. Moreover, because the conditions of annealing during IR pyrolysis and heat treatment are different, the temperature of cyclization is much lower than the above-described DSC data. During IR pyrolysis, all the studied samples successively change color from white to yellow, brown, and black; at the same stage of annealing, the tints of colors of the (co)polymers prepared in different solvents were different.

The dynamics of change in the structure of PAN during IR pyrolysis was described in [41]. The formation of the system of conjugated bonds is registered spectrally from the emergence of new absorption bands due to the stretching vibrations of C=N and C=C bonds at 1583, 1490, 1370, and 1275 cm^{-1} and due to stretching vibrations ν_{CH} at the double bond (3066 cm^{-1}). Simultaneously, the intensity of the absorption band corresponding to the bending vibrations of CH_2 groups in the main chain of PAN (1450 cm^{-1}) decreases, and during the formation of conjugation, the absorption band corresponding to the stretching vibrations of nitrile groups ($\nu_{C\equiv N}$) splits into two maxima: the first is at 2243 cm^{-1} (nitrile groups in the initial PAN), and the second is at 2200 cm^{-1} (nitrile groups involved in conjugation with PCS fragments). When annealing is completed (200°C), the PCS is characterized by a common spectral envelope in the range 1370–1000 cm^{-1} and the maxima of absorption bands are not defined and are shifted toward the longwave region. Absorption bands due to the end nitrile groups and residual CH_2 groups manifest themselves very weakly or are not registered at all in the IR spectrum. For incomplete conjugation or its short regions, maxima of absorption bands in the IR spectrum are observed below 1500 cm^{-1}: at 1370, 1250, and 1150 cm^{-1}. The spectra of PCSs of these samples show absorption bands corresponding to nitrile groups and CH_2 moieties.

At a temperature of IR pyrolysis of 200°C, the maximum changes in the IR spectra and, hence, in the structuring of the samples are observed for PAN synthesized in $ZnCl_2$ (Fig. 4, curve *5*) and DMSO (curve *1*). A sharp decline in the intensity of the absorption band ν_{CN}, its splitting into two maxima, the almost total absence of the individual absorption band corresponding to the bending vibrations of CH_2 groups at 1450 cm^{-1}, and the smoothed contours of absorption bands in the longwave region provide evidence for a high degree of conjugation. Note that similar changes occur in the reference PAN sample (Aldrich, curve *6*). Particular emphasis should be focused upon the spectrum of the PCS of the sample prepared in a solution of sodium thiocyanate (curve *4*), which strongly differs from the other spectra. The absorption bands due to thiocyanate are preserved during the IR pyrolysis of PAN even at 200°C; however, a reduction in their intensities at the initial stages of IR pyrolysis

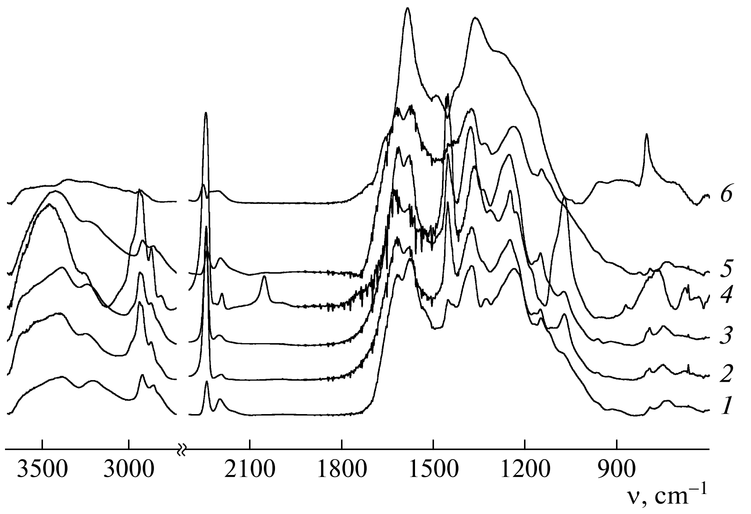


Fig. 4. IR spectra of homopolymers synthesized in (*1*) DMSO, (*2*) DMF, (*3*) water, and (*4*, *5*) aqueous solutions of (*4*) NaNCS and (*5*) $ZnCl_2$ after IR pyrolysis at 200°C; (*6*) the IR spectrum of pyrolyzed PAN (Aldrich) is shown for comparison.

may imply that salt groups are involved in the formation of PCS.

With consideration for the partial hydrolysis of PAN synthesized in the aqueous solution of zinc chloride to form amide and acidic groups and the general tendency toward an increase in conjugation in the copolymers containing acidic and/or ester groups [30], it may be inferred that the hydrolysis of the homopolymer is favorable for the formation of PCSs. On the other hand, in all IR spectra of the PCSs (at 200°C) other than the reference PAN sample, two maxima are observed in the area of 1600 cm^{-1}: at 1620 and 1575 cm^{-1}. In addition, the absorption bands of C=C–H groups (1380 and 805 cm^{-1} [50]) feature low relative intensities in comparison to those of the IR spectrum of the PCS in the reference sample. This fact may suggest that the amount of C=N bonds prevails over the amount of C=C bonds in the PCSs of the studied PAN samples; that is, the formation of conjugation systems stops at the stage when blocks or regions containing a large amount of V_N defects may exist in the system [42].

It is known [50] that chlorides of transition metals (Co, Gd, and Fe) affect the structure of the PCS: chlorides of Fe and Co, when incorporated into the pyrolyzed PAN, form π–*d* and *n*–*d* donor–acceptor complexes with nitrile groups of the polymer [50]. Complexed nitrile groups are uninvolved in the cyclization reaction; therefore, the stage of formation of conjugated bonds C=N is excluded. Sequences of conjugated double bonds formed as a result of dehydration of the main chain of the polymer are longer than conjugation sequences obtained in the absence of transition-metal salts. The use of intense IR radiation facilitates the acceleration of carbonization processes and the formation of a developed polyconjugation system; the level of order in this system is determined by the intensity of IR radiation.

In contrast, in this study, because of the effect of the medium of synthesis, which manifests itself as several factors, including the partial hydrolysis of polymers, during the formation of the PCS even at 200°C, C=C bonds are formed at a low rate. (In the above-cited study of pyrolysis of PAN-based composites containing transition-metal chlorides, the structure of the PCS free of C=N bonds was observed even at 160°C.) Therefore, formation of the PCS and, accordingly, the amount of C=N double bonds (V_N-defects) in it may be controlled. This circumstance may be important, for example, for attainment of the maximum adsorption of oxygen atoms on the surfaces of PAN monolayers, a circumstance that contributes to a shift in conductivity of the adsorption complex toward the electronic side [42].

During the IR pyrolysis of AN–MA binary copolymers (Fig. 5), the first spectral signs of PCS formation are somewhat different from those of the homopolymer: new absorption bands, which are assigned to the stretching vibrations of C=N and C=C bonds in the conjugation system, are registered at 1584–1587 and 1485 cm^{-1}, and simultaneously, the intensity of the absorption band at 1450 cm^{-1}, which corresponds to the bending vibrations of CH_2 groups of the PAN backbone that are not involved in conjugation, decreases. In addition, the absorption band appears at ~1370 cm^{-1} and the intensities of bands at 3400, 1600, and 800 cm^{-1} increase. These changes occur in the samples at different temperatures of IR pyrolysis, for example, at 140°C in water and at 160°C in DMSO, DMF, and the solution of sodium thiocyanate.

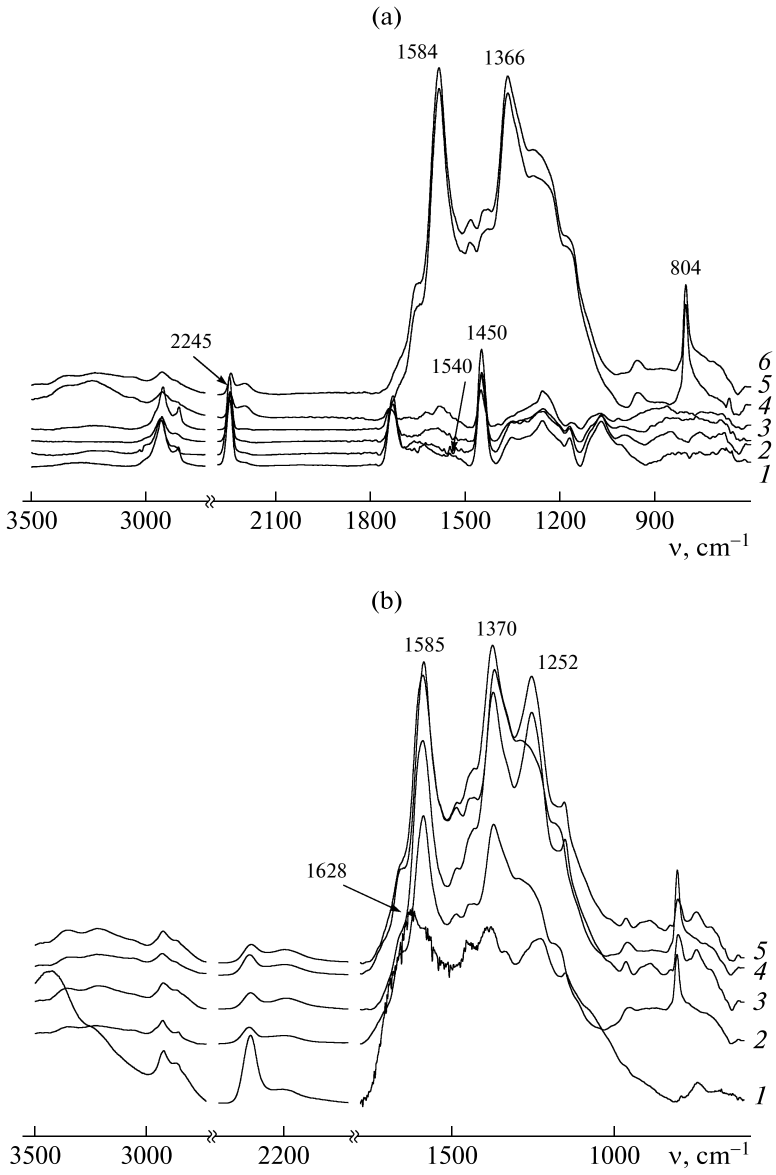


Fig. 5. ATR IR spectra of AN–MA copolymers before and after IR pyrolysis: (a) the copolymer synthesized in water at (*1*) 20, (*2*) 100, (*3*) 140, (*4*) 160, (*5*) 180, and (*6*) 200°C; (b) $T = 200$°C, copolymers prepared in (*1*) an aqueous solution of $ZnCl_2$, (*2*) DMSO, (*3*) an aqueous solution of NaNCS, (*4*) water, and (*5*) DMF.

The above data are in agreement with the results of DSC measurements; the onset temperature of the exo-effect increases in the same sequence of solvents.

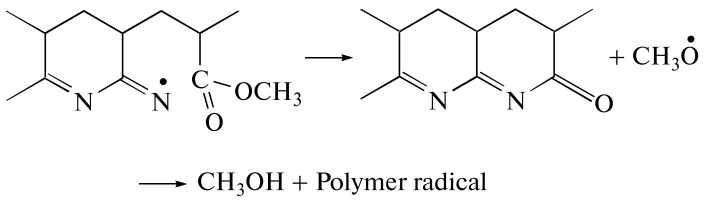
The appearance of absorption bands typical for the PCS is accompanied by a decline in the intensity of the absorption band due to the stretching vibrations of nitrile groups in the initial copolymer (ν_{CN}, 2245 cm^{-1}). Its maximum first slightly (by 1.5 cm^{-1}) shifts toward the shortwave region and then shifts to the longwave region, and at a temperature of IR pyrolysis of 180°C, the band splits into two maxima: 2239–2241 cm^{-1} and a shoulder at 2195–2197 cm^{-1}. This behavior of the absorption band is typical for all the studied samples; the same behavior was observed for AN–MA–itaconic acid terpolymers [31]. Simultaneously, the intensity of absorption increases in the shortwave region (above 3000 cm^{-1}), where the stretching vibrations of NH and C=C bonds are registered. Moreover, during heating, the intensity of the absorption band due to the stretching vibrations of the ester group of MA (ν_{CO}, 1730 cm^{-1}) decreases and new bands appear in the IR spectrum at 1670–1680 cm^{-1}. These results ate consistent with the literature data about the thermal pyrolysis of AN–MA copolymers that were prepared via suspension polymerization [28]. Figure 5a shows the IR spectra that are registered at various temperatures of IR pyrolysis for the AN–MA copolymer prepared via precipitation polymerization in water and illustrate the above changes.

There is a difference in the IR spectra of PSCs that have already formed in binary copolymers (Fig. 5b). For the samples synthesized in DMSO (curve *2*) and water (curve *4*), the IR spectra of PCSs show two intense maxima at 1584 and 1366 cm^{-1} and, in the range below 1300–1000 cm^{-1}, general increases in the intensities of the absorption bands are seen, as is typical for long conjugation sequences. By the end of heat treatment (200°C), the IR spectra of the copolymers synthesized in DMF (curve *5*) and in the aqueous solution of sodium thiocyanate (curve *3*) feature all signs of PCSs with short conjugation sequences: absorption bands with well-defined maxima are observed at 1584, 1370, 1253, and 800 cm^{-1}, and the intensity of the absorption band in the shortwave region (<3000 cm^{-1}) increases.

Note that, for the AN–MA copolymer synthesized in the aqueous solution of zinc chloride, the structure of the PCS is different (curve *1*). The absorption region of conjugated bonds is broader than those of other copolymers: the spectrum of the PCS shows a shortwave absorption band at 1628 cm^{-1} and a longwave band at 1223 cm^{-1}, the ratio of intensities of the main bands is almost the same, and there is no absorption band at 800 cm^{-1}. With allowance for the fact that the IR spectrum of the initial sample exhibits the absorption bands of acidic groups, which may arise as a result of partial hydrolysis, it may be supposed that the PCS contains oxygen-containing structures and that the amount of C=N bonds increases relative to that of other samples.

An increase in the content of MA units in the copolymer synthesized in DMF affects the thermal behavior of the copolymer during IR pyrolysis: at the initial stage of the formation of conjugation (160°C), the absorption band due to the stretching vibrations of nitrile groups shifts toward the longwave region in a symbate manner with an increase in the fraction of MA in the copolymer; for the sample containing 5.4 mol % MA, this shift amounts to 5 cm^{-1}. For IR pyrolysis at 200°C, a marked difference is observed in the IR spectra of the polymers: the longwave band due to the mixed vibrations of C=N and C=C bonds in the sample containing 5.4 mol % MA splits into two maxima at 1609 and 1580 cm^{-1}, the absorption maxima at 1390 and 1251 cm^{-1} shift toward the shortwave region, and the ratio of intensities of these bands is reversed with respect to those of the copolymers containing a smaller amount of MA units. Hence, the increase in the fraction of MA in the copolymer leads to a decrease in the length of conjugation in the chain.

On the basis of the above data, the following conclusions can be made. The key effect of the conditions of synthesis of the AN–MA binary copolymers, specifically the reaction medium, may be reduced to the effect on the conformational structure of the elementary unit; the resulting effect on the configuration order of the polymer chain; and, finally, the effect on the structure formation of PCSs (Fig. 5b). In accordance with the literature data, the intramolecular radical cyclization reaction of nitrile groups is terminated on the ester group of MA, but the growth of the kinetic chain continues via the reaction of chain transfer involving a methoxy radical and a new macromolecule [28].



Hence, MA units do not show any marked blocking effect on the reaction of nitrile groups. As a consequence, the exo-effect on the DSC curves becomes broader and its intensity declines [28], and an increase in the amount of MA units leads to the formation of the PCS with short conjugation sequences.

In terms of the structure of the PCS, the studied copolymers may be divided into two groups. The first group is composed of the copolymers in which PCSs with long conjugation sequences (water, DMSO, and $ZnCl_2$) are formed by the end of the heat treatment, a phenomenon that may be explained by the presence of ionized carboxyl groups (water as a solvent) in macromolecules, the absence of any noncovalent interactions between the solvent and polymer (DMSO), and the compositional heterogeneity of the copolymer formed in water. The second group includes copolymers with short conjugation sequences (DMF, sodium thiocyanate), a circumstance that is apparently related to interactions between the solvent and the functional groups of macromolecules.

The incorporation of a small amount of itaconic acid into a macromolecule exerts a strong effect on the conditions of formation and the structure of the PCS, as estimated from the IR spectra with respect to the IR spectra of the AN–MA binary copolymers.

Changes in the ATR IR spectra of terpolymer samples are evident even at a temperature of IR pyrolysis of 100°C: the absorption band peaking at 1780 cm^{-1} appears and then disappears at higher temperatures;

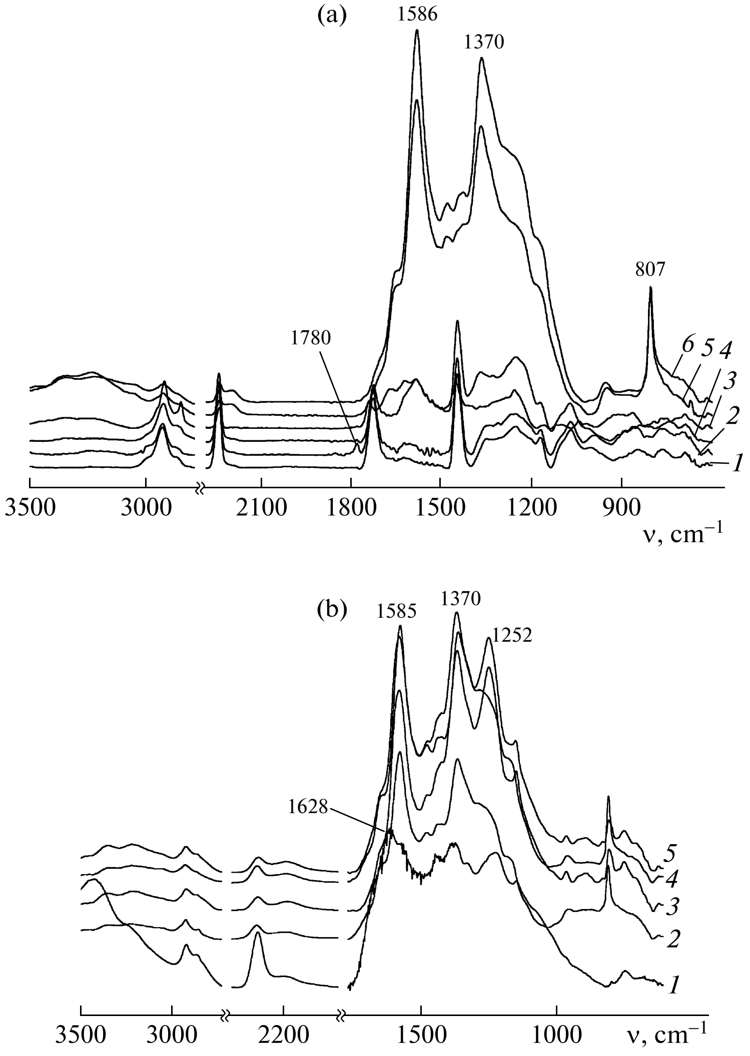
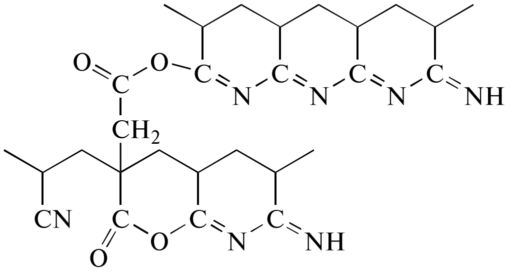


Fig. 6. ATR IR spectra of AN–MA–itaconic acid copolymers before and after IR pyrolysis: (a) the copolymer synthesized in water at (*1*) 20, (*2*) 100, (*3*) 140, (*4*) 160, (*5*) 180, and (*6*) 200°C; (b) $T = 200°C$, copolymers prepared in (*1*) an aqueous solution of $ZnCl_2$, (*2*) DMSO, (*3*) DMF, (*4*) water, and (*5*) an aqueous solution of NaNCS.

the contour of the absorption band at 1730 cm^{-1} becomes asymmetric, and its intensity declines (Fig. 6a). This outcome testifies to the complex character of chemical processes occurring during thermolysis of the terpolymer and formation of cyclic structures as intermediates: anhydride and imide with different positions of C=O bonds [29, 31].



At higher temperatures, changes are observed for the absorption band corresponding to the stretching vibrations of nitrile groups in the initial terpolymer (ν_{CN}, 2245 cm^{-1}). Similarly to the above-described spectra of binary copolymers for IR pyrolysis at 180°C, this band splits into two maxima; new absorption bands with maxima at 1586, 1480, and 1370 cm^{-1} emerge; the intensity of the absorption band at 1450 cm^{-1} declines; and the intensities of the absorption bands at 3400, 1650, and ~800 cm^{-1} increase.

The IR spectra of the copolymers prepared in various solvents are characterized by a number of different features (Fig. 6b). For example, the formation of the PCS for the terpolymer synthesized in water occurs via the formation of inter- and intrachain cyclic structures that facilitate conjugation and, hence, cause a decrease in the onset temperature of its formation. However, the final structure of the PCS is analogous to that described above for the binary copolymer: long conjugation sequences and weak maxima of the absorption bands in the IR spectrum of the sample below 1300 cm^{-1}.

In the case of the terpolymers isolated from organic solvents, the PCS is formed similarly to that of the sample synthesized through precipitation polymerization via the mechanism including the formation of cyclic structures as intermediates or interchain carbonyl groups. In this case, the system contains shorter conjugation sequences: well-defined maxima of the absorption band are seen in the IR spectrum of the PCS below 1370 cm^{-1}. An increase in the amount of MA units in the copolymer has almost no effect on the conditions of formation and the structure of the PCS: the onset of formation of the conjugation system and its structure are practically the same. Hence, the incorporation of itaconic acid into the copolymer eliminates the effect of the content of MA on the structure of the PCS.

During the formation of the PCS in the terpolymer synthesized with the participation of sodium thiocyanate, no absorption bands of carbonyl groups, which suggest the formation of any anhydride or other cyclic structures, are found. The relative intensity of the absorption band at 1250 cm^{-1} is lower than that for the binary copolymer. As a result under the same conditions of pyrolysis, the level of conjugation for the ternary copolymer is higher or the regions of conjugated bonds are longer than those for the binary copolymer.

For the terpolymer synthesized in the aqueous solution of $ZnCl_2$ and subjected to partial hydrolysis during synthesis, the PCS is formed similarly as that for the binary copolymer synthesized under the same conditions: the formation of cyclic oxygen-containing structures may be proposed from the presence of absorption bands at 1628 and 1233 cm^{-1} in the IR spectra.

On the basis of the aforementioned evidence, the following conclusions can be made. The completeness of conjugation during the formation of PCSs in terpolymers is influenced by several factors: the state of carboxyl groups in itaconic acid and the conformational and structural changes in a chain that appear during the synthesis. For example, in the terpolymer prepared via precipitation polymerization, carboxyl groups are nonionized and no traces of water are observed in the initial IR spectrum; as a result, PCSs are characterized by long conjugation sequences. For the terpolymer isolated from the aqueous solution of sodium thiocyanate and containing ionized carboxyl groups, shorter conjugation sequences are formed in the absence of the residual solvent, whereas the simultaneous existence of partially ionized carboxyl groups and trace amounts of residual solvent in the terpolymers synthesized in organic solvents leads to additional shortening of PCS regions owing to defects in the primary structure of the polymer that are related to the noncovalent interactions of CH-groups in the backbone [52].

On the whole, in the case of the terpolymers, PCSs are formed via intermediate carbonyl-containing structures (cyclic or interchain).

CONCLUSIONS

An analysis of the published data and results of this study shows that, other conditions being the same, the rate of thermal cyclization should increase in the following sequence: terpolymer (AN–MA–itaconic acid), AN homopolymer, binary copolymers (AN–MA). This tendency may be rationalized by the accelerating effect of acidic groups on the initiation of the cyclization reaction [29] and by the deterioration of the regular structure of chains after the incorporation of the acrylate monomer into them [28].

However, the conditions of synthesis may strongly affect the thermal behaviors of PAN and its copolymers. The factors that can effect changes in the rate of thermal cyclization and the PCS structure are as follows: (i) the presence of residual solvent (DMF) noncovalently bound with the hydrogen atom of the CH-group in the main chain of PAN, a situation that promotes inhibition of the involvement of neighboring methylene groups in the conjugation, promotes the formation of bonds via π electrons of the nitrile group, and leads to an increase in the amount of nitrogen that is in the PCS ($ZnCl_2$) or is involved in the formation of PCS (NaNCS); (ii) the partial conversion (hydrolysis) of nitrile groups into carboxyl and/or amide groups; (iii) the state of the carboxyl group of itaconic acid (ionization, dimerization, etc.); and (iv) the compositional heterogeneity of the copolymer.

The PCS with the long conjugation system and a small amount of defects is formed if the polymer contains acidic and/or amide groups and there are no noncovalent interactions between the residual solvent and a macromolecule (polymers synthesized in water or DMSO) and if the structure of the macromolecule is regular (incorporation of monomers unable to initiate cyclization disturbs the regular structure of the PCS). In contrast, during the interaction of residual solvent (DMF or sodium thiocyanate) with the polymer chain, the PCS contains a number of short conjugation sequences of various kinds separated by methylene or nitrile groups. The PCSs of this type are typical also for terpolymers that contain cyclic or pseudocyclic structures formed by acidic groups of itaconic acid.

Thus, variation in the conditions of synthesis (the choice of solvent, the type and the amount of comonomer, and allowance for the occurrence of hydrolysis during formation or isolation of the polymer) makes it possible to affect the thermal behavior of AN-based copolymers, namely, the rate of formation and the structure of the PCS.

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