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THERMOOXIDATIVE DECOMPOSITION OF NITRILE COPOLYMERS CONTAINING ITACONIC ACID UNITS

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IR spectroscopy showed that in nitrile copolymers and fibres containing units based on itaconic acid, these units can exist in different modifications. The formation and set of modifications are a function of the conditions of preparation of the copolymer and fibre, especially their hydrophilicity. The existence of different modifications of itaconic acid fragments (in both the initial samples and in the samples formed in the initial stages of heat treatment) affects the rate of the subsequent processes of thermooxidative decomposition of the objects and the set of polyconjugated systems formed and consequently also the supermolecular structure. These findings should be taken into consideration both in the analysis of the corresponding copolymers and in the technology of their fabrication and processing.

Thermooxidative stabilization of fibres based on copolymers of acrylonitrile is an important stage in fabrication of carbonized materials. Acrylonitrile copolymers are used as the raw material for carbon materials, and for this reason, it is important to study the effect of comonomers on thermooxidative processes from the point of view of purposive alteration of the initial structure of the raw material to obtain carbon material with defined properties [1-9]. Industrial fibres and films are based on acrylonitrile (AN), methylacrylate (MA), and itaconic acid (IA). The role of MA units in thermal stabilization of the fibres were investigated in [3, 6, 10]. It was hypothesized that these units do not participate in chemical reactions in the initial stage of heat treatment; their role is reduced [6, 10] to removal of the stresses that arise during cyclization.

It was shown in [11] that incorporation of units with carboxyl groups in the molecular chain of acrylic polymers activates cyclization processes at nitrile groups during heat treatment. The concentration of IA units, for example, in the structure enriches the polymer with oxygen and ensures hydrophilicity; water affects the change in the functional activity of both carboxyl and nitrile [9] groups. All of these factors together affect the occurrence of thermooxidative decomposition of AN copolymers.

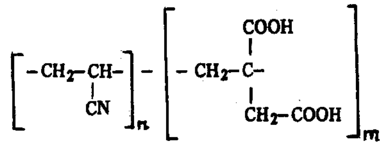
We investigated samples of AN, MA, and IA copolymers and fibres. Their composition is reported in Table 1.

Samples 1, 3, and 6 were obtained by suspension polymerization with an activator: potassium permanganate/oxalic acid for sample 1, potassium persulfate/sodium metabisulfite for samples 3 and 6. The specific viscosity of the samples was: 1) 1.30; 3) 1.70; 6) 1.75. The fibres were spun by the wet method from dimethylformamide solutions. Samples 2, 4, and 5 were industrial samples, and their density was 1170, 1210, and 1190 kg/m^3, respectively.

The IR spectra of the samples were obtained on a UR-20 spectrometer in KBr pellets (relative to KBr pellets). Heat treatment was conducted in a thermostat at 180 ± 2°C.

The x-ray structural studies (small-angle) were conducted on a KRM-1 setup. CuKα radiation was used. The distribution of the intensity in the meridional direction (in photographing the fibres) was recorded with a BR21 recording unit.

The structure of AN:IA copolymers is usually represented as



$$\left[-CH_2-\underset{CN}{CH}-\right]_n-\left[-CH_2-\overset{COOH}{\underset{CH_2-COOH}{C}}-\right]_m$$

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TABLE 1. Ratios of the Optical Densities of a Series of Absorption Bands and Optical Density of the 2940 cm^{-1} Band (D_i/D_{2940}) in the IR Spectra of Starting Samples of Polymers and Fibres

Sample No.	Composition, mole %	Form	D_i/D_{2940} and assignment of i absorption bands [12]		
			D_{3450}/D_{2940} ν (OH) of water	D_{2240}/D_{2940} ν (C≡N)	D_{1740}/D_{2940} ν (C=O) of esters and dicarboxylic acids
1	AN : IA , 98 : 2	Powder	0,69	1,96	0,88
2	AN : MA, 95 : 5	Fibre	0,39	2,03	1,43
3	AN · IA , 97,8 : 2,2	Same	0,26	2,01	0,70
4	AN : MA : IA , 92,3 : 6,2 : 1,5	»	0,56	1,82	1,69
5	Same	»	1,43	1,79	1,68
6	AN : MA : IA , 94,5 : 3,5 : 2,0	»	0,17	1,67	1,67

However, it was shown in [13] that the carboxyl groups of the IA component can be transformed (especially in the presence of water) into different structures during copolymerization, storage, and especially during heat treatment of the samples. For example, as a result of transformation of one carboxyl group, the acid fragment goes from dibasic to monobasic. Formation of anhydride cross-links, lactone rings [13], and conversion of carboxyls to the ionized form are possible.

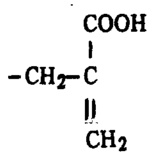
The purpose of the studies was to determine the effect of the difference in the real structure of the copolymers from their formula composition on the subsequent evolution of thermooxidative processes.

The results of processing the IR spectra of the initial samples (powders and fibres) are reported in Table 1: the ratios of the optical densities of a series of absorption bands to the optical density of the 2940 cm^{-1} absorption band [ν_{as} (CH_2)]. In the discussion below, each sample will be given the number indicated in Table 1. The vibrations of carbonyls, ester, and acid groups contribute to the 1740 cm^{-1} absorption band in the spectra of ternary copolymers.

It follows from the data in Table 1 that the hydrophilicity of the samples, estimated with the numerical value of D_{3540}/D_{2940} is different and it is not a direct function of the number of dicarboxylic acid units. In addition, the amount of bound water in industrial samples 4 and 5, which have the same composition, differed significantly (the IR spectra were recorded relative to KBr pellets prepared at the same time as the samples). The slight difference in the numerical values of D_{2240}/D_{2940} could not only be due to the different concentration of units with a nitrile group but also to the characteristics of formation of associates between them in the different copolymers, which affects the intensity of the 2240 cm^{-1} absorption band, as established in [14]. The IR spectra of a series of initial and heat-treated samples are shown in Figs. 1 and 2.

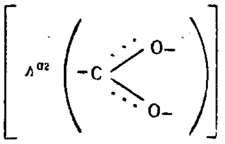
The analysis of the spectra of the starting samples showed that an absorption shoulder at 1690 cm^{-1} related to vibrations of carbonyl groups in α-, β-unsaturated chain fragments (they can be acid, aldehyde, or ketone groups [12]) is characteristic of samples 3, 4, and 6.

It is completely possible that the absorption at 1690 cm^{-1} in the IR spectra of the starting samples is direct confirmation of partial decarboxylation in units with IA in copolymerization or fabrication of fibres, leading to the formation of structures of the type [13, 15]



$$-CH_2-\overset{\overset{\displaystyle COOH}{|}}{\underset{\underset{\displaystyle CH_2}{\|}}{C}}$$

Absorption is observed at 1590 cm^{-1} in the spectra of starting fibres 4 and 5



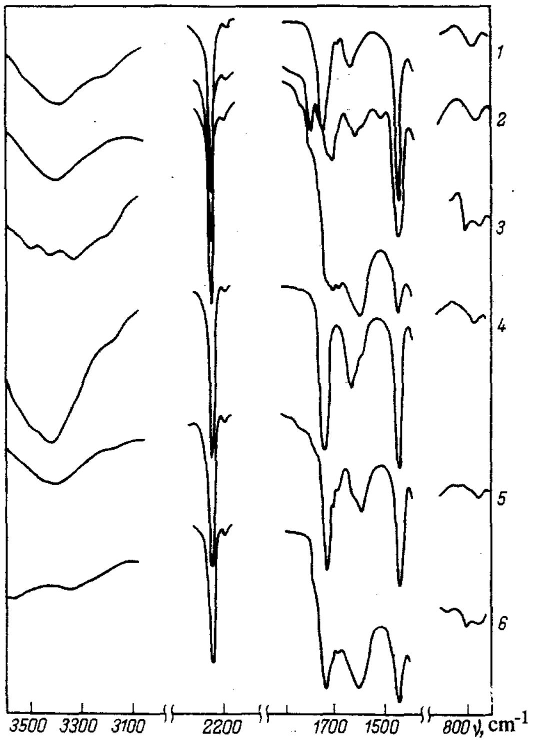


Fig. 1. IR spectra of initial and heat-treated samples 1 and 5: 1) initial sample 1; 2, 3) sample 1 treated with heat at 180°C for 0.5 and 3 h; 4) initial sample 5; 5, 6) sample 5 treated with heat at 180°C for 0.5 and 4 h.

i.e., the formation of an ionized form of carboxyl groups is possible. We also note the appearance of absorption at 1780 cm^{-1} due to the existence of anhydride cross-links in the spectra of initial samples 3 and 6. In these samples, the concentration of water is minimal and the formation of ionized carboxyl groups was not established.

Absorption also appeared at 1630 cm^{-1} in the spectra of all initial samples in the region examined, to which the δ(OH) of water basically contributed. Even based on the spectra of the initial samples, we can thus say that the IA-based units are partially modified during fabrication or storage. These units are especially significantly modified in heat treatment of the samples (Figs. 1 and 2), and we can thus hypothesize that oxidation at nitrile groups takes place relatively weakly in the initial stages of heat treatment (for example, 30 min at 180°C) [16] and all of the changes in the spectra in the region of vibrations of carboxyl and carbonyl groups are primarily due to modification of IA units.

The data in Figs. 1 and 2 suggest that the intensity of the 1740 cm^{-1} absorption band decreases in the spectra of samples 1 and 3 as the duration of heat treatment increases, accompanied by the appearance of and an increase in the intensity of the absorption bands at 1720 and 1705 cm^{-1} and the appearance of a band at 1780 cm^{-1}. This could be because the dibasic IA fragment becomes monobasic during heating, initially in the presence of an H bond (1720 cm^{-1} band) and then without this kind of bond (1705 cm^{-1}) as a consequence of consumption of carboxyls for formation of anhydride bridges (1780 cm^{-1}) and due to their participation in nucleophilic activation of cyclization [11] of the nitrile groups in the polymer. Polyconjugated structures (PCS) [16] increase in the fibre much more slowly than in the copolymer powder judging by the intensity of the absorption bands in the 1600-1580 and 815 cm^{-1} region in the spectra of sample 1, heated for 3 h, and sample 3, heated for 6 h (Fig. 2). This could be attributed to the different hydrophilicity of the samples (see Table 1).

When water is present in the copolymer, the reaction of hydrolysis of anhydride bridges occurs during heat treatment, free carboxyl groups are formed as a result, and the mobility of the chains increases, in the final analysis leading to more intense formation of PCS. With a low concentration of water in the sample, hydrolysis is inhibited, there are few free COOH groups, and PCS systems develop more slowly. The spectra of the AN:MA:IA fibres (samples 4-6) differ for both the initial samples and the heat-treated samples. A significant number of anhydride bridges is identified in comparatively less hydrophilic sample 6 even after 6-h heat treatment and the band of vibrations of free carboxyl groups does not appear at all.

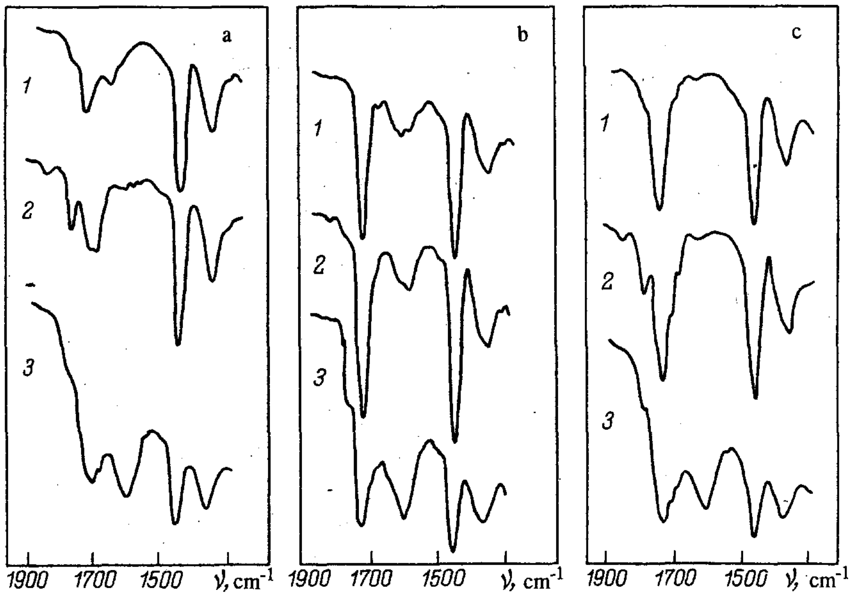


Fig. 2. IR spectra of initial and heat-treated samples 3, 4, and 6: a: 1) initial sample 3; 2, 3) sample 3 treated with heat for 0.5 and 6 h; b: 1) initial sample 4; 2, 3) sample 4 treated with heat for 0.5 and 4 h; c: 1) initial sample 6; 2, 3) sample 6 treated with heat for 0.5 and 6 h.

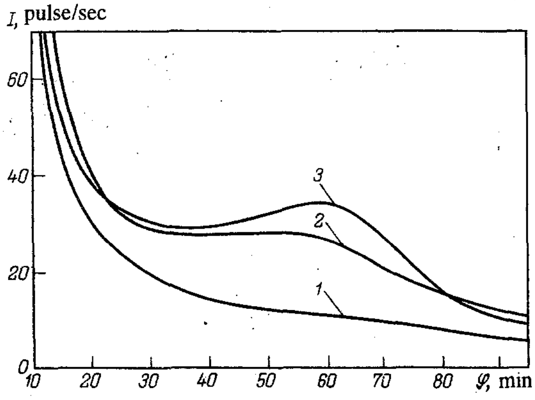


Fig. 3. Distribution of the intensity of x-ray radiation in the meridional direction for heat-treated samples 2 (1), 4 (2), and 5 (3).

The kinetics of the intensity of absorption of anhydride groups and formation of PCS in heat treatment of samples 3 and 6 probably have a certain similarity. Significantly fewer anhydride cross-links and more unbound COOH groups are identified spectroscopically as a result of heat treatment in more hydrophilic samples 4 and 5, whose initial structure contains ionized carboxyl groups; as indicated above, this causes a higher rate of formation of PCS, and this rate is higher in more hydrophilic sample 5. Formation of PCS is not identified in the spectra of sample 2, treated with heat for 6 h. This indicates the higher thermal stability, at least in the initial stage of heat treatment, of nitrile fibres containing no IA units [3, 10]. This is also confirmed by the results of small-angle x-ray scattering studies: a small-angle reflection indicative of structural transformations of the chain of the copolymer [17] appears in samples 4 and 5 in heat treatment for 6 h at 180°C, while the small-angle reflection is missing in sample 2 and only appears with a significant duration of heat treatment (Fig. 3).

The IA units in the chains of the macromolecules can thus exist in both the unchanged dibasic form and in the ionized or monobasic (free or bound by a H bond) form, and they can also be transformed into anhydride bridges and α-, β-unsaturated carbonyl-containing structures. Modification of IA units is a function of the hydrophilicity of the samples to a significant degree.

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