THERMAL DEGRADATION OF RANDOM COPOLYMERS OF ACRYLONITRILE WITH α-METHYLSTYRENE

II. ANALYSIS OF THE REACTION PRODUCTS

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The thermal decomposition of binary copolymers of acrylonitrile with variable amounts of α-methylstyrene (2—40%) has been studied at $p = 10^{-2} - 10^{-4}$ torr and $T = 0 - 600°$. The decomposition products (solids, liquids and gases) have been characterized by IR and UV spectroscopy, gas chromatography, vapor pressure osmometry and elemental analysis. The decomposition mechanism has been ascertained on the basis of the obtained results.

Improvement of the tinctorial and hydrophilic properties of polyacrylonitrile (PAN) fibres may be achieved by introduction through copolymerization of functional groups, which will interact more easily than the nitrilic group with dyes or water. However, the comonomer has the same effect as any structural irregularity, so that, generally, the comonomer may be introduced only within certain limits without the basic properties of the homopolymer being decisively altered.

The thermal behaviour, one of these basic properties, of the binary copolymers (*BC*) of acrylonitrile (*AN*) with vinyl acetate (*VA$_c$*) or α-methylstyrene (*MS*) was first examined by TG and DTA and it was established that the introduction of *VA$_c$* has a lower effect than *MS* on the thermal stability of *PAN*, and also that the sequence distribution plays an important role.

Since the methods used offered no conclusive data concerning the reaction mechanisms, in the present paper the thermal degradation of *BC* of *AN* with *MS* was studied via the pressure variation due to the evolved volatiles in a high-vacuum system (EGA method), the reaction products being trapped and then characterized by various analysis methods.

Experimental

The *BC* of *AN* with 0—40% w/w of *MS* were prepared by suspension polymerization, using the redox initiation system of persulphate—metabisulphite. The comonomer was estimated spectrophotometrically and by the Kjeldahl method.

Thermal degradation was carried out in a degradation high-vacuum installation with continuous evacuation and trapping of the volatile products. The equipment

is similar to those described by McNeill [1], with the only difference that the space for the sample holder and the oven were in a horizontal position, so that the thermocouple could be introduced into the centre of the sample. The sample about 300 mg, was distributed uniformly in a thin layer in a flat vessel. The heating rate was $10°/min$ and the pressure of the system incrased from the initial value of 10^{-5} torr to at least 10^{-1} torr, due to the evolved volatiles. These were trapped at liquid nitrogen temperature and then passed by heating and detent from the traps to collectors, which could be easily detached from the equipment for analysis of the reaction products by other methods.

The following products were formed:

(a) condensable and uncondensable volatiles at liquid nitrogen temperature;

(b) liquid and/or solid products deposited at the outlet of the oven (cooled with cold water), the so-called "cold fraction";

(c) a solid residue in the reaction vessel.

The "cold fraction" was quantitatively soluble in dimethylformamide (DMF).

The reaction products were characterized by IR on a Perkin-Elmer 577 and UV on a Unicam SP 800 spectrometer, by gas chromatography on a Siemens L-400 gas chromatograph provided with a flame ionization detector, by vapour pressure osmometry on a Knauer osmometer and by elemental analysis.

The calibration of the Knauer osmometer was carried out with trimethylbenzene in DMF at $110°$ and a sensitivity of 32, the concentration of the solutions varying between 0.2 and 2 g/100 ml, the same conditions being applied to the solutions of the studied samples.

For the gas chromatographic analysis of the reaction products, the following operational conditions were used: the chromatographic column (2×3 mm i.d.) was packed with Chromosorb W ($80-100$ mesh) coated with 15 w/w $\%$ Silicone SE-52; the column temperature was programmed from 50 to $180°$ with a heating rate of $7°/min$; argon was used as carrier, at a rate of 18.0 ml/min.

The IR spectra were recorded on KBr tablets, and the UV spectra on DMF solutions of the reaction products with a constant concentration of 0.24 g/l.

Results and discussion

Typical pressure variation curves during the thermal degradation of the studied copolymers (expressed in mV as indicated by the Pirani gauge) are shown in Fig. 1 a and b, the first group of curves (A) referring to the whole quantity of volatiles, and the second (B) only to the gases uncondensable at liquid nitrogen temperature.

The curves of the BC with a content up to 14 w/w $\%$ MS show no essential differences compared to that of PAN (Fig. 1a), but with increasing MS content a more and more pronounced peak arises at $325-450°$, together with one at $25-150°$, due probably to the elimination of the residual comonomer MS (Fig. 1b). Consequently, the thermal stability of the BC may be serously affected by the increasing MS content.

Figure 2 shows the temperatures of maximum decomposition rates (T_m) for the different stages of decomposition as functions of the *MS* content, suggesting important differences, especially in the third and fourth degradation steps, again especially at *MS* contents higher than 14 w/w %.

The amounts of the degradation products, together with the number of components in the gas fraction and the average molecular weight of the "cold fraction", are presented in Table 1.

Table 1

Results of thermal degradation of PAN and of BC with MS

Sample	Solid residue w/w, %	"Cold fraction" w/w, %	Volatiles w/w, %	Average molecular weight of the "cold fraction", M	Number of components in the liquid fraction
PAN	15.51	32.56	51.93	306.5	9
BC2.4MS	22.9	43.66	33.44	336	7
BC7.8MS	19.89	36.30	44.81	322.21	7
BC10MS	23	51.73	25.27	444.4	13
BC14MS	26.01	60.71	13.28	351.5	
BC15MS	14.65	68	17.35	390.8	—
BC20MS	21.6	56.73	21.67	436.3	—
BC30MS	24.25	35.72	40.33	440.3	16
BC35MS	14.68	43.11	42.21	457.03	—
BC40MS	9.8	45.1	45.1	—	18

If the amount of the residue shows no specific modifications, that of the "cold fraction" indicates a maximum, and that of the volatiles a minimum for the *BC* with 14−15 w/w % *MS*.

An essential modification of the thermal behaviour of the *BC* with a 15−20 w/w % *MS* content was also observed by TG [2, 3] and pyrolysis − gas chromatography [4]. The unlike structure of the degradation products of the studied copolymers is well evidenced in the IR spectra and confirmed by gas chromatography. Even in the carbonaceous residue the IR spectra indicate the presence of structures which are the more complex, the higher the comonomer content (Fig. 3).

Elemental analysis of the residue also gave different values for the copolymers with *MS* contents up to 15 w/w %: 17.18% N, 75.44% C, 1.34% H and 6.16% O (corresponding to an overall formula $C_{16}N_3H_3O$) and for those with higher *MS* contents: 20% N, 55−60% C, 2−2.5% H and 11% O ($C_{15}N_3H_6O_3$). The oxygen is absorbed from the air, when the residue is taken out, with the formation of nitrone [5].
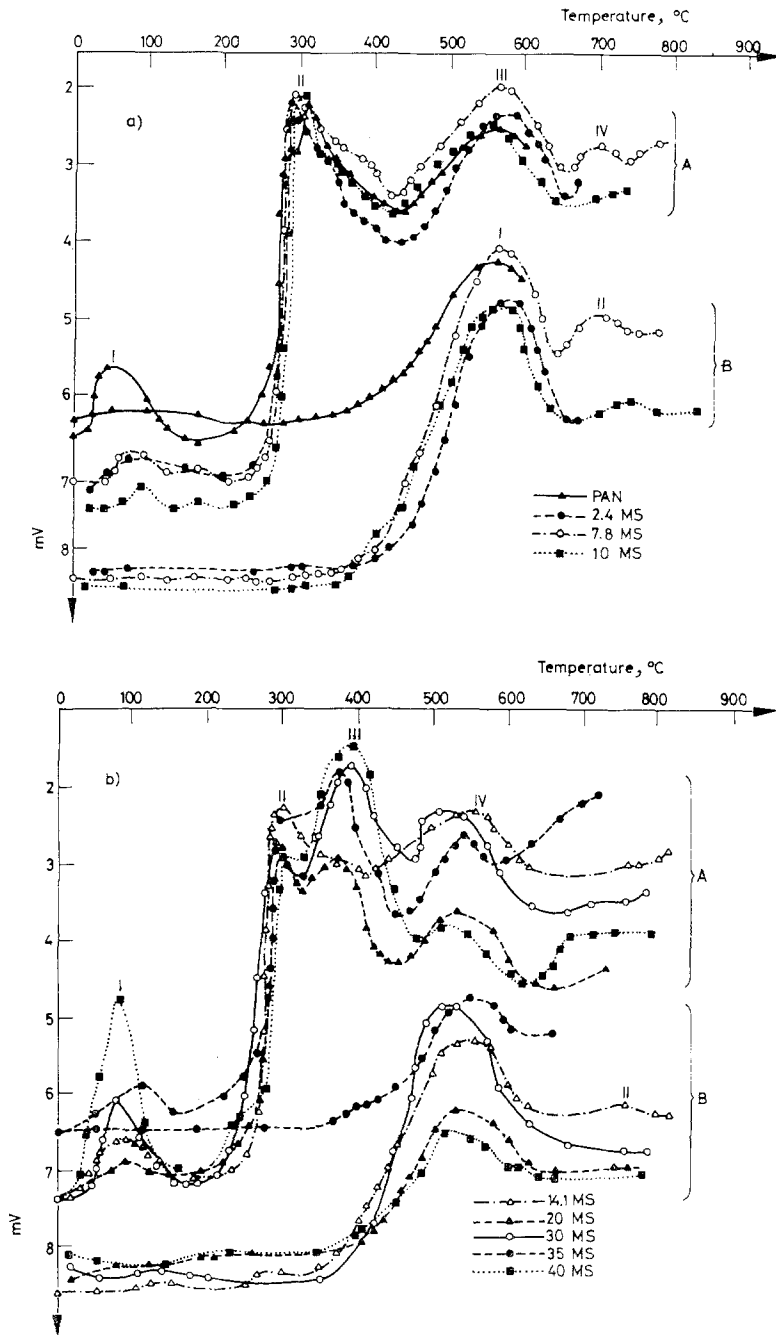
Fig. 1. Pressure variation curves as functions of temperature: a, *PAN* and BC with 2.4 *MS*, 7.8 *MS* and 10 *MS* b, *BC* with 14.1 *MS*, 20 *MS*, 30 *MS*, 35 *MS* and 40 *MS*

The IR spectra of the residue seem to support this conclusion, showing more acecntuated wide bands and the specific three maxima for aromatization in the $1100-1700$ cm^{-1} region [6] (Fig. 3) for residues of copolymers with lower MS contents. In contrast, the copolymers with higher MS contents show two supplementary bands, at 700 and 760 cm^{-1}, the intensity increasing with the MS content, which may indicate either the presence of double bonds in alkenes and benzene derivatives or that of pyrimidinic structures [7].
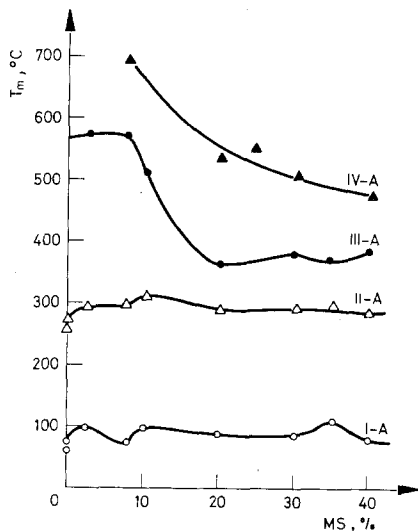
Fig. 2. Temperature corresponding to maximum decomposition rate versus BC composition

The "cold fraction" may be a brownish solid at the outlet of the oven, or a yellow fluid at a greater distance from the oven. The IR spectra are quite similar, irrespective of aspect, except that the bands in the $700-800$ cm^{-1} and $3020-3090$ cm^{-1} regions are more accentuated for the fluids. Typical IR spectra for various BC are shown in Fig. 4.

Again, essential differences are connected especially to the comonomer content of the copolymers, the differences appearing mainly in the $700-800$ cm^{-1}, $1000-1200$ cm^{-1}, $2200-2300$ cm^{-1} and 3500 cm^{-1} regions, the intensity of the bands increasing with the comonomer content. On the other hand, the decrease of the 1565 cm^{-1} band relating to $C=N$ conjugation and the presence of $-NH$ groups, suggest a decrease of the probability of internal cyclization of the nitrilic groups, responsible for the well-known colouring of PAN on heating above 220°. The more accentuated conjugation by $C=N$ groups in the copolymers of lower MS content is also confirmed by the decrease with increasing MS content of the 360 mm band which corresponds to heterocyclic compounds with nitrogen, or to aromatic compounds with amino groups [8] (Fig. 5).
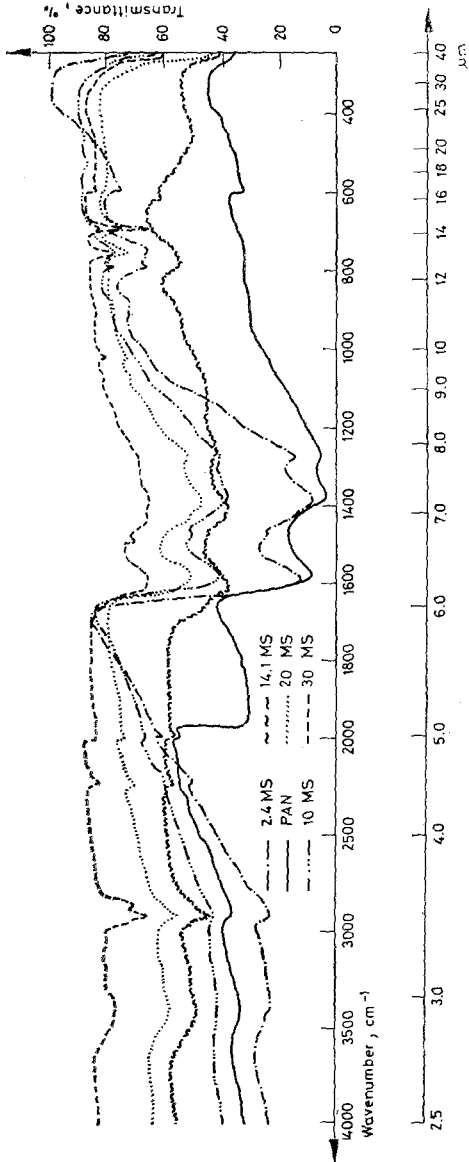
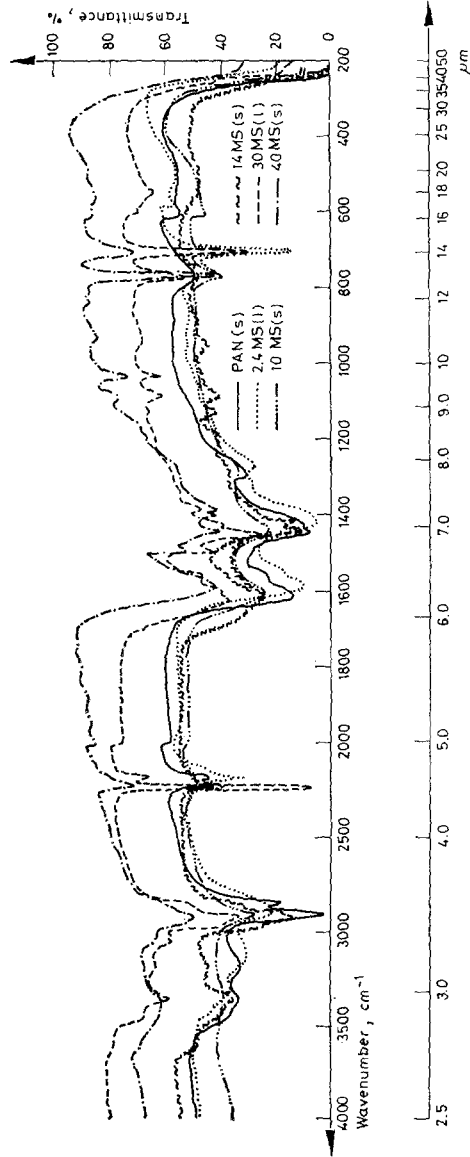Fig. 3. IR spectra of residues obtained at 800° by thermal degradation of BC with various compositions

Fig. 4. IR spectra of solid (s) or liquid (l) condensate in the "cold fraction" obtained at 800° by thermal degradation of BC with various compositions

Therefore, during the thermal degradation of the copolymers of *AN* with *MS*, besides the volatiles, fragments with aromatic structure with $M = 350-450$ are formed, either by cyclization of the nitrile groups, or by chain scission of the *MS* units, the probability of the latter increasing with the *MS* content. These fragments condense to give the "cold fraction".
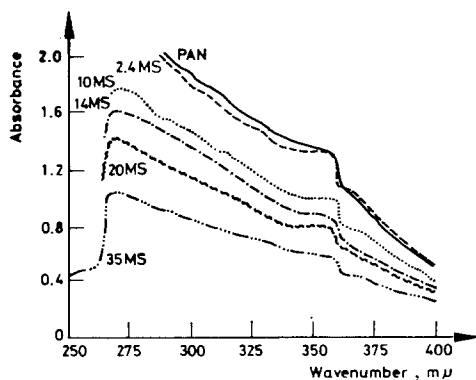

Fig. 5. UV spectra of the "cold fractions" obtained at 800° by thermal degradation of *BC* with various compositions
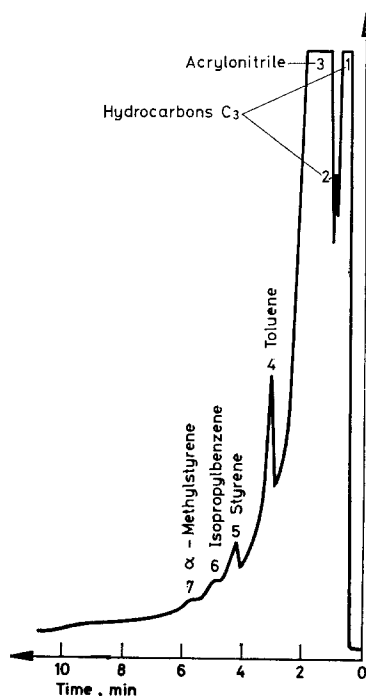

Fig. 6. Liquid fraction chromatogram of *BC* 2.4 *MS*

The volatiles trapped at liquid nitrogen temperature may be separated by heating in vacuum to room temperature in a gas phase and a liquid phase. These two phases were analysed separately by gas chromatography and some typical chromatograms of the liquid phase are shown in Figs 6 − 8.

These chromatograms of the liquid phase were considered representive for the modifications which occur in the degradation mechanism, while the composition of the gas phase depends mainly on the volatility of the reaction products at room temperature and may therefore not be characteristic.
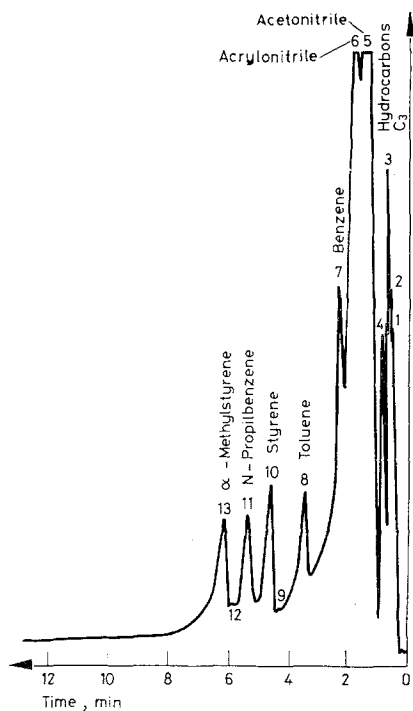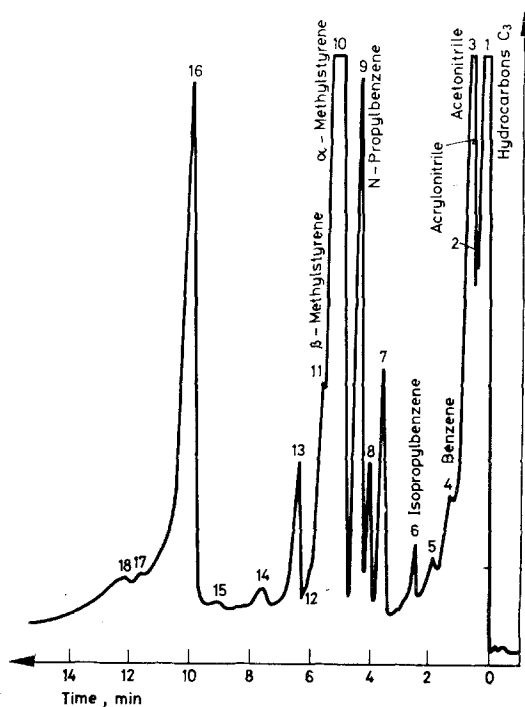

Fig. 7. Liquid fraction chromatogram of BC 10 MS

Fig. 8. Liquid fraction chromatogram of BC 40 MS

The thermal degradation of PAN also gives HCN and NH_3, but these compounds could not be identified because of the use of a flame ionisation detector [9], while the uncondensed gases may be H_2, N_2 and CH_4 [10].

The influence of the comonomer on the thermal degradation mechanism of the comopolymer is well known [11], and in the case of AN copolymers with butadiene [12] and isobutene [13] have been studied. The specific behaviour of the AN/MS copolymers is probably due to the chemical nature of the MS units and the characteristics in the sequence distribution, explained by the difference between the reactivity constants.

It has been shown that, due to the differences between the reactivity constants, the ability of the successive *MS* units to *AN* units is very great and the presence of *MS* sequences with lengths of more than one is very small [14], so the reaction mechanism can be presented as follows (Scheme 1):
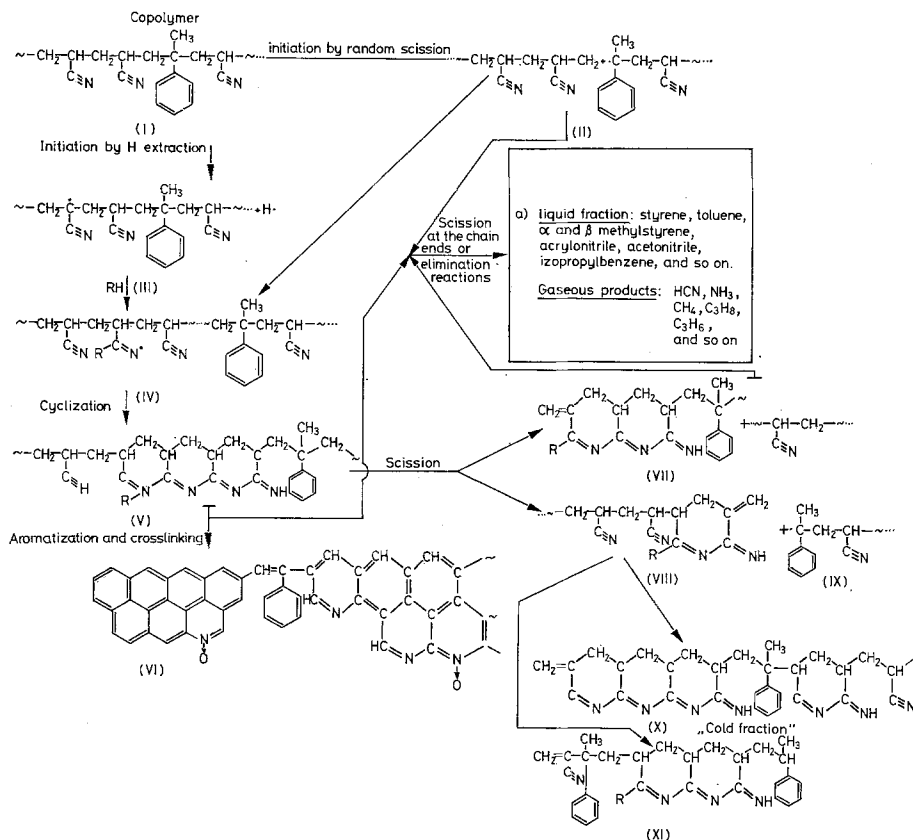
The decomposition reaction is initiated either by proton extraction from the tertiary carbon or by random scission. The obtained radicals could lead to the colouring of the polymer by nitrile group cyclization, or to crosslinking, resulting in intermediate products. *MS* interferes with the nitrile group polymerization reaction and could remain in the residue structure. The solid residue can be obtained by an advanced aromatization and the solid or liquid "cold fraction" is formed by scission reactions at random sites of the chain. The gaseous and liquid compounds are formed by β-scission at the chain-ends.

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Résumé — On a étudié la décomposition thermique des copolymères binaires de l'acrylonitrile avec des quantités variables d'α-méthylstyrène (2—40%), à $p = 10^{-2} - 10^{-4}$ torr et $T = 0—600°$. Les produits de décomposition (solides, liquides et gaz) ont été caractérisés par spectroscopie IR et UV, chromatographie en phase gazeuse, osmométrie sous pression de vapeur et analyse élémentaire. Le méchanisme de décomposition a été établi à partir des résultats obtenus.

Zusammenfassung — Die thermische Zersetzung der binären Kopolymere von Akrylnitril mit verschiedenen Mengen von α-Methylstyrol (2—40%) wurde bei $p = 10^{-2}—10^{-4}$ Torr und $T = 0—600°$ untersucht. Die Zersetzungsprodukte (Festkörper, Flüssigkeiten und Gase) wurden durch IR- und UV-Spektroskopie, Gaschromatographie, Dampfdruck-Osmometrie und Elementaranalyse charakterisiert. Der Zersetzungsmechanismus wurde an Hand der erhaltenen Ergebnisse bestätigt.

Резюме — Термическое разложение бинарных сополимеров акрилонитрила с различным количеством (2—40%) α-метилстирола было изучено при $p = 10^{-2}—10^{-4}$ торр и $T = 0—600°$. Продукты разломения (твердые, жидкости и газы) были охарактеризованы ИК- и УФ-спектроскопией, газовой хроматографией, газонаполненной осмометрией и элементарным анализом. На основании полученных результатов выведен механизм разложения.