INFRARED SPECTROSCOPIC STUDY OF THE PRODUCTS OF THERMAL DEGRADATION OF POLYAMIDES IN INERT ATMOSPHERE

Miroslav SVOBODA[a], Bohdan SCHNEIDER[b] and Jan ŠTOKR[b]

[a] *Forensic Institute of Public Security, 182 00 Prague 8*
[b] *Institute of Macromolecular Chemistry,*
Czechoslovak Academy of Sciences, 162 06 Prague 6

Infrared spectra were measured of condensates generated by heating polyamide-6, polyamide-12, polyamide-11, polyamide-8 and polyamide-6,6 in inert atmosphere at 300, 350, 400, 500, and 600°C for various time. The products of thermal degradation were characterized by infrared spectroscopy. It was found that the thermal history of polyamide degradation can be detected from infrared spectra.

The mechanism of thermal degradation of macromolecular compounds is of interest both from the point of view of basic reserach of polymer reactions, but also for purely practical reasons, for example for determining the applicability ranges of plastics, their ecological degradation, or efficient utilization of plastic wastes in the role of secondary raw materials, etc. Particularly the polyamides have been the subject of numerous studies described in the literature. Appreciable changes of the physico--chemical properties of aliphatic polyamides occur at temperatures above 200°C in absence of oxygen. During pyrolysis of mixed polyamides based on hexamethylene adipamide, only water, CO, CO_2 and lower hydrocarbons pass into the gas phase, as well as cyclopentanone which reacts with amines forming a Schiff base[1-5].

Ballistreli et al.[6] have shown that in polyamides at 380°C, β-C—H transfer occurs together with the formation of olefinic and amide end groups, yielding nitrile groups, when water can be eliminated. For polyamide-6, depolymerization is the typical process, with the establishment of an equilibrium between polyamide-6 and ε-caprolactam. The higher the molecular weight of the polymer, i.e. the smaller the number of end groups, the lower is the depolymerization process[7-9]. At room temperature, ε-caprolactam forms a hydrogen-bonded dimer, with *cis*-amide bonds, in contrast to the *trans*-amide groups in linear chains. Luderwald et al.[10] assume that cyclic products of thermal degradation at 170°C are formed not only from polyamide-6, but also from polyamide-4, polyamide-7, polyamide-12, polyamide-6,6, polyamide-

-6,10, polyamide-4,10, polyamide-11,6, and polyamide-12,12. According to these authors, linear degradation products are formed at temperatures exceeding 400°C.

Do et al.[11] have measured FT IR spectra of polyamide-6 and polyamide-6,6 at 150 and 200°C, and after cooling to ambient temperature in nitrogen atmosphere. Difference spectra indicated both reversible and irreversible changes in polyamide-6 and polyamide-6,6 at these temperatures. With increasing temperature, the content of free N—H groups was enhanced. From the time-dependence of changes in IR spectra at 200°C it was found that during annealing, only the intensity ratio of the conformationally sensitive bands, I_{936}/I_{1148}, is changed with polyamide-6,6, and the crystallinity-sensitive ratio I_{930}/I_{1123} with polyamide-6. The intensities of the bands of the crystalline phase — I_{936} for polyamide-6,6, and I_{930} for polyamide-6 — remain constant or increase slightly, while the intensites of the bands of the amorphous phase — I_{1148} for polyamide-6,6 and II_{1123} for polyamide-6 — are found to decrease. Do et al.[11], as well as many other authors assume that also the structure with a *trans-vinylene* group is formed during degradation.

From the above review it is evident that so far nobody has performed a detailed analysis of the condensation products of thermal degradation of polyamides at higher temperatures, or investigated the time and temperature variation of the changes in their chemical composition. It has been the aim of the present work to determine, by means of infrared spectrophotometry, the behaviour and structural changes of aliphatic polyamides in nitrogen atmosphere in dependence on the duration of the effect of various temperatures.

EXPERIMENTAL

Materials for thermal degradation: polyamide-6, Spolamid ZP (PA-6, density 1 123 kg/m³), polyamide-6,6 filled with glass, Technyl A218V25 (PA-6,6, density 1 233 kg/m³), polyamide-8 prepared in the laboratories of the Prague Institute of Chemical Technology (PA-8, density 1 042 kg/m³), polyamide-11 filled with 8% of graphite, Rilsan BMN GBT (PA-11, density 1 033 kg/m³), and polyamide-12 Grilamid L20 GMN (PA-12, density 956 kg/m³).

Degradation process. The polymer samples (5 g) were thermally degraded in an apparatus of our own construction as described in ref.[12]. The required temperature was maintained with an accuracy of ±5°C, the flow of nitrogen was maintained at 20 ml/min. After the predetermined time of thermal degradation, the vessel with the polymer was cooled to room temperature by a stream of air within about 5 min.

The infrared spectra of polymers and of the thermally degraded samples were measured with the spectrometer Perkin–Elmer 983G, with a resolution of 3 cm⁻¹, in the range 4 000—300 cm⁻¹. The KBr technique was applied, using 1·5 mg of polymer per 150 mg of KBr and a die 13 mm in diameter. The studied polyamide was repeatedly ground and pressed with a part of the KBr batch. It was found that for obtaining a homogeneous mixture and reproducible results, it is sufficient to repeat this process five times. The remainder of KBr was then added and the pellet prepared for measurement. All studied samples were treated in this way.

RESULTS AND DISCUSSION

The wavenumbers in infrared spectra of the measured polyamides are shown in Table I. The data of refs[13–15] were used for band assignment. The measured spectra

TABLE I

Band wavenumbers and assignment for the measured polyamides (PA, see Experimental)

Band assignment	Wavenumber, cm^{-1}				
	PA-6	PA-8	PA-11	PA-12	PA-6,6
$\nu(NH)$	3 300	3 301	3 301	3 297	3 299
Fermi resonace: $2\times$ Amide II and $\nu(NH)$	3 077	3 080	3 079	3 081	3 078
$\nu_a(CH_2)$	2 928	2 925	2 918	2 919	2 927
$\nu_s(CH_2)$	2 858	2 850	2 848	2 848	2 855
Amide I	1 648	1 641	1 648	1 642	1 641
	1 642				
Amide II	1 559	1 545	1 546	1 554	1 535
	1 536				
$\delta(CH_2)$, N-vicinal	1 473		1 465	1 464	1 472
$\delta(CH_2)$	1 461	1 463	1 454		1 461
$\delta(CH_2)$	1 434	1 433	1 434	1 434	1 433
$\delta(CH_2)$, CO-vicinal	1 416	1 416	1 417		1 416
$\gamma_w(CH_2)$	1 371	1 371	1 371	1 369	1 370
$\gamma(CH_2)$		1 320	1 337		
$\gamma(CH_2)$			1 295		
Amide III + $\gamma_w(CH_2)$ + $\gamma_t(CH_2)$			1 277	1 268	1 272
Amide III + $\gamma_w(CH_2)$ + $\gamma_t(CH_2)$	1 261	1 255	1 259		
Amide III + $\gamma_w(CH_2)$ + $\gamma_t(CH_2)$		1 240	1 242	1 239	
Amide III + $\gamma_w(CH_2)$ + $\gamma_t(CH_2)$	1 199		1 222	1 220	1 198
$\nu(CC)$, $\nu(C_\alpha N)$, $\gamma_t(CH_2)$		1 195	1 190	1 190	1 179
$\nu(CC)$, $\nu(C_\alpha N)$, $\gamma_t(CH_2)$	1 168	1 162	1 157	1 159	
$\nu(CC)$, $\nu(C_\alpha N)$, $\gamma_t(CH_2)$	1 121	1 120	1 122	1 120	1 139
$\nu(CC)$, $\nu(C_\alpha N)$, $\gamma_t(CH_2)$	1 077	1 020	995	1 064	1 052
Amide IV-$\delta(CONH)$	1 028				
Amide IV-$\delta(CONH)$	980				
Amide IV-$\delta(CONH)$	960	941	937	943	934
Amide IV-$\delta(CONH)$	928				
$\gamma_t(CH_2)$	729	724	721	721	729
Amide V	693				692
Amide VI	577	584	582		581
Amide VI	521		544	537	
$\delta(CCC)$	444	466	492	470	498
$\delta(CCC)$			443	420	
$\delta(CCC)$			407		405
Amide VII		357	351		356

were treated with the Perkin–Elmer 3700 Data Station. For spectra presentation, the function FLAT was used to straighten the baseline, and the function ABEX for band intensity adjustment. The spectra in the ranges $3\,200-2\,700$, $2\,400-2\,180$ and $1\,800-600\ cm^{-1}$ are shown in Figs $1-2$. The band intensities in Tables $II-III$ were determined by the baseline method at the band maximum, and referred to standardized sample weight of $1\cdot5$ mg of polymer[12]. From the obtained values, the intensity ratios were then calculated for band pairs selected to assess polymer degradation.

To calculate the percentage of generated monomer in the condensate of degraded polyamide-6 at temperatures 400, 500 and 600°C, the program RATIO (for quantitative analysis of mixtures) was applied. In the case of polyamide-6, the peak intensity of the Amide II band at $1\,536\ cm^{-1}$, in the case of ε-caprolactam the peak of Amide IV at $980\ cm^{-1}$ were used in the calculation.

Polyamide-6 (PA-6)

Spolamide ZP was subjected to thermal degradation at 300 and 600°C for $0\cdot5$, 1, 2 and 4 h (Fig. 1, Table II). According to the data published by Dechant et al.[13] the measured spectrum corresponds to the α-modification of PA-6. The bands at $1\,648$ $1\,558$ and $980\ cm^{-1}$ correspond to the γ-modification which in a small amount is always present.
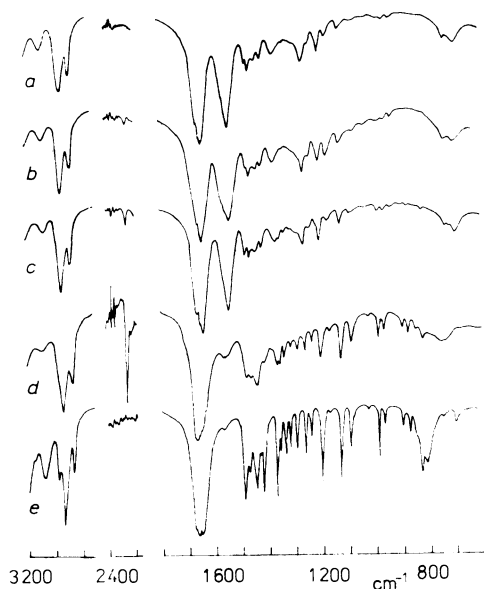

FIG. 1

Infrared spectra of polyamide-6 and its condensed degradation products after one hour of heating: *a* unheated polymer, *b* 400°C, *c* 500°C, *d* 600°C, *e* ε-caprolactam (unheated monomer)

After one hour of thermal treatment at 300°C, the IR spectrum of polyamide-6 does not practically exhibit any change. A slight enhancement of the Amide IV band at 928 cm^{-1} corresponding to the crystalline component, together with the slight reduction of the band intensity at 1 121 cm^{-1} corresponding to the amorphous component indicates, in agreement with the results of Do et al.[11], an increase in the crystallinity of the studied sample (Table II).

In IR spectra of samples heated at 400°C, a new band appears at 2 244 cm^{-1}, assigned to the vibration of a nitrile group[14]. After four hours of degradation the IR spectrum exhibits further new bands at 1 233 and 1 309 cm^{-1}. The band at 1 233 cm^{-1} is assigned to the twisting vibration of a methylene group[10], and the band at 1 309 cm^{-1} to a methylene group wagging vibration[14]. Band intensities are reduced at 1 473 cm^{-1} (bending vibration of the methylene group vicinal to nitrogen), 1 416 cm^{-1} (bending vibration of the methylene group vicinal to carbonyl), and at 1 028 cm^{-1} (Amide IV — bending vibration of the –CONH– group); at the same time, however, no strong bands of the ε-caprolactam dimer are observed (e.g. bands at 985 or 1 368 cm^{-1}), indicating that thermal degradation at 400°C leads not only to depolymerization, but also to the splitting of any amide group in the chain by β-C—H hydrogen transfer leading to nitrile group formation (Fig. 1, Table II). The intensity of the band of the –CONH– group bending vibration at 928 cm^{-1} (Amide IV — crystalline phase) is higher after 0·5 h of heating at 400°C than after

TABLE II

Intensities in the band maxima (I), band intensity ratios, and contents of polyamide-6 (PA-6) and ε-caprolactam (ε-CL) in nonvolatile products of the thermal degradation of PA-6. Assignment: I_{928} Amide IV band, I_{1085} ε-CL backbone stretching vibration, I_{1121} complex vibration of backbone carbon atoms and methylene groups, I_{1536} Amide II, I_{2244} nitrile group band

| Heating | | I_{928} | I_{1085} | I_{1121} | I_{1536} | I_{2244} | I_{928} | I_{2244} | PA-6 | ε-CL |
C	h			.10^3			I_{1121}	I_{1536}	wt. %	
—	—	230	0	610	1 244	0	0·377	0	100	0
300	1	250	0	570	1 194	0	0·438	0	100	0
400	0·5	350	0	510	1 015	0	0·686	0	93·8	6·2
400	1	270	0	700	949	3	0·386	0·032	92·4	7·6
400	2	260	0	780	899	5	0·333	0·056	89·8	10·2
400	4	80	0	840	883	9	0·095	0·102	87·4	12·6
500	0·5	260	470	1 190	911	10	0·218	0·110	90·3	9·7
500	1	160	490	1 230	889	12	0·130	87·8	12·2	
500	2	70	550	1 240	792	14	0·056	0·177	82·6	17·4
500	4	0	760	1 330	382	18	0	0·471	60·6	39·4
600	1	0	880	1 460	184	26	0	1·413	36·8	63·2
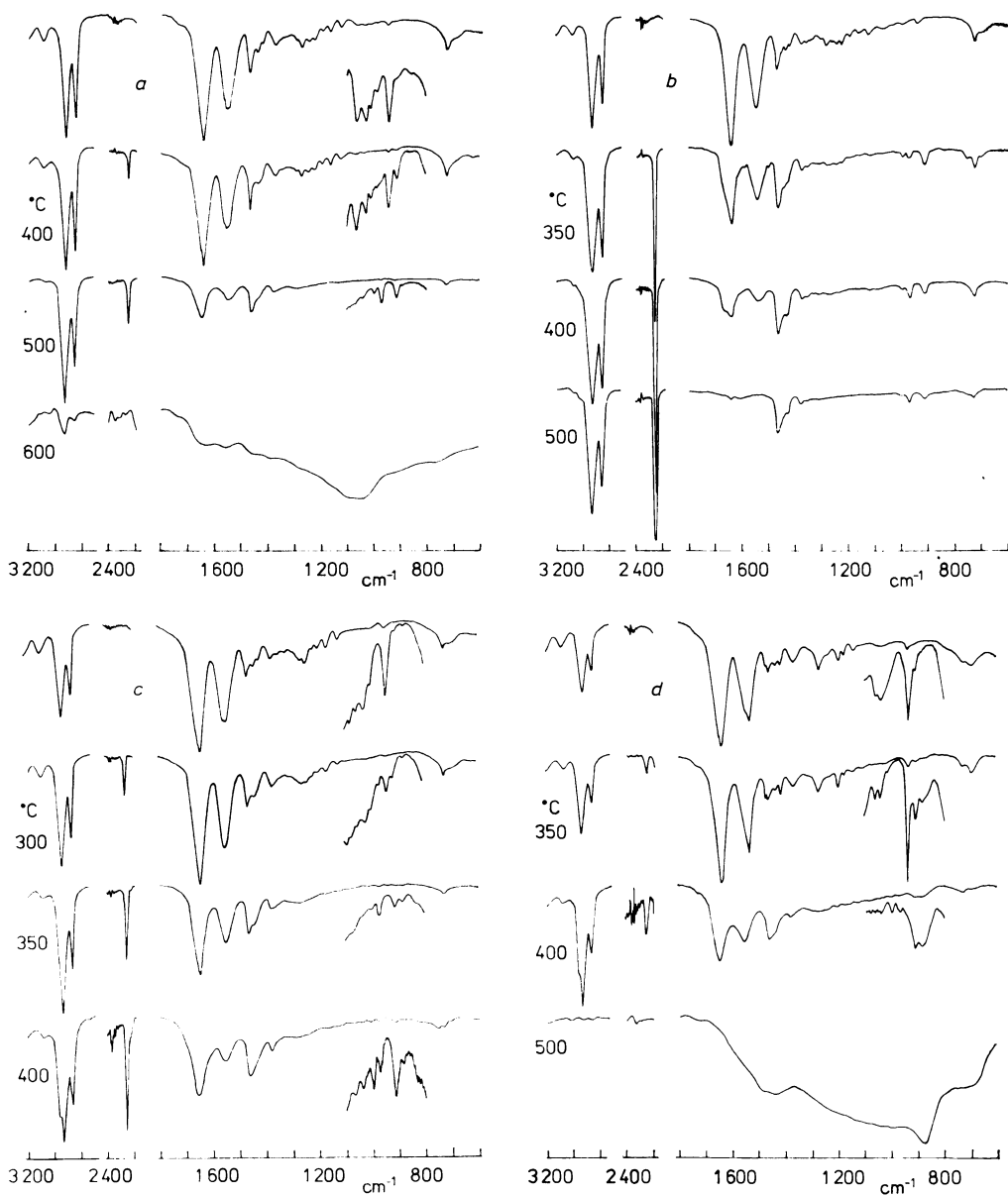
FIG. 2

Infrared spectra of polyamides (PA) and of its condensed degradation products after one hour of heating (T, °C): a PA-12, b PA-11, c PA-8, d PA-6,6. The spectrum of unheated polymer is shown as the first from top. In the ranges $2\,400-2\,140$, $1\,100-800\;\mathrm{cm}^{-1}$, spectra are magnified by a factor of 12

1 h of heating at 300°C, but it decreases rapidly with increasing time of heating. The band intensity of the skeletal stretching vibration at 1 121 cm^{-1} is lower after 0·5 h of heating at 400°C than after 1 h of treatment at 300°C, but it gradually increases with prolonged heating time. The band intensity ratio I_{928}/I_{1121} characterizing the crystallinity degree of polyamide attains a maximum after 0·5 h of heating at 400°C, but decreases later on.

When the degradation temperature is 500°C, further new bands appear at 320, 398, 493, 818, 867, 893, 1 085, 1 256, 1 284, 1 308, 1 332, 1 351 and 1 365 cm^{-1}. A comparison of the IR spectra of polyamide-6 degraded for one hour at 500°C with the IR spectrum of ε-caprolactam (monomer) reveals that all the new bands, as well as the bands with increased intensity in the range 2 000—300 cm^{-1} correspond to ε-caprolactam. At the same time, the intensities of the Amide I, Amide II and Amide IV bands at 1 648, 1 536 and 920 cm^{-1} are reduced (Fig. 1, Table II).

With prolonged heating time, the aggregation state of the degradation products is changing. After the first half-hour of degradation, the polyamide still remains to be solid; after one to two hours at 500°C, a liquid fraction is formed besides the solid; after four hours of degradation, the polymer has the consistence of vaseline. The amount of ε-caprolactam generated among the degradation products was evaluated by means of the RATIO program. The liquid fraction after one hour of heating contains about 60% of ε-caprolactam, and this content remained practically unchanged even after two hours of degradation. The contents of ε-caprolactam and PA-6 in the solid products and in the vaseline residue are shown in Table II. These data indicate that depolymerization prevails over random chain splitting. This is also supported by the low band intensity of the nitrile group which is formed by random chain splitting with β-C—H hydrogen transfer.

At 600°C, overall destruction of the polymer chain takes place, as indicated by the high intensities of the bands which have gradually appeared already at temperatures of 400 and 500°C. Moreover, the bending vibration band of the –NHCO– group in the crystalline phase at 928 cm^{-1} is completely missing, the Amide II band at 1 536 cm^{-1} is very weak, and on the methylene group stretching vibration band there appears a shoulder at 2 950 cm^{-1} corresponding to a stretching vibration of methyl groups. In the range of nitrile group stretching vibrations there appears a band at 2 214 cm^{-1} which can be assigned to a nitrile group in a system conjugated with a C=C double bond[14] (Fig. 1). A comparison of the IR spectrum of PA-6 degraded at 600°C for one hour with the IR spectrum of ε-caprolactam indicates that the liquid degradation product of PA-6 is composed of ε-caprolactam dimers and liquid hydrocarbons with nitrile groups (Fig. 1, Table II).

Polyamide-12 (PA-12)

Grilamid L20 GMN was thermally degraded at 300 and 600°C for one hour, and at 400 and 500°C for 0·5, 1, 2 and 4 h (Fig. 2a, Table III).

After one hour of thermal treatment at 300°C, the IR spectrum of PA-12 does not practically exhibit any change. However, a slight intensity reduction of the Amide band at 1 554 cm^{-1} and of the methylene group rocking vibration indicates some loss of *trans*-amide groups and splitting of polymer chains. In analogy with ref.[11] we have assigned the Amide IV band at 943 cm^{-1} to the respective vibration in the crystalline phase of the polymer, and the band at 1 120 cm^{-1} to the stretching vibration of the chain backbone in the amorphous phase. An increase of the intensity ratio I_{943}/I_{1120} indicates an enhancement of polymer crystallinity due to melting (Table III).

With samples heated at 400°C, after one hour of degradation the IR spectra exhibit new bands at 909 and 2 244 cm^{-1}. After two hours of degradation a further band appears at 966 cm^{-1} (Fig. 2a, Table III). The band at 909 cm^{-1} corresponds to a vinyl group vibration[14], the band at 966 cm^{-1} is assigned to the vibration of a trans--vinylene group[14], and the band at 2 244 cm^{-1} corresponds to the vibration of a nitrile group[14]. The intensity of the vinyl, *trans*-vinylene and nitrile group bands increases with prolonged heating time. The intensity of the Amide II band at 1 554 cm^{-1} and of the rocking vibration band of methylene groups at 721 cm^{-1} changes in inverse proportion to the heating time. The band intensity ratio I_{943}/I_{1120} used to characterize the crystallinity of polyamide-12 attains its highest value after one hour of degradation at 400°C and decreases afterwards; this indicates that with short heating recrystallization occurs after cooling, but with longer heating times, chain degradation occurs and the amorphous phase becomes predominant. The changes in the IR spectra of PA-12 which appear after heating at 400°C indicate that in the degradation process, *trans*-vinylene groups are formed, as well as olefin and amide end groups, giving rise to nitrile groups[6].

At the temperature of 500°C, with PA-12 prolonged heating time leads to a rapid intensity reduction of the Amide I and Amide II bands at 1 642 and 1 554 cm^{-1}, while the Amide III, Amide IV and Amide VI bands are no longer apparent in the IR spectrum of the thermal degradation product of PA-12 (Fig. 2a). After one half-hour of degradation, the intensities of the vinyl group band at 909 cm^{-1} and of the nitrile group band at 2 244 cm^{-1} were sharply enhanced, but with prolonged heating time their intensities begin to decay. After one and two hours of degradation, the band of the *trans*-vinylene group is higher than the vinyl group band. This could be explained by an enhanced contribution of the radical mechanism to degradation (Table III). A new band appears at 1 375 cm^{-1}, assigned to the methyl group bending vibration[14], overlapping the methylene group wagging vibration at 1 369 cm^{-1}. Simultaneously, the methylene group vibration band is enhanced and shifted from 1 464 to 1 460 cm^{-1}. The ratio of band maximum intensities of the nitrile group and Amide II bands, I_{2244}/I_{1554}, and of the methylene group bending vibration and Amide II bands, I_{1460}/I_{1554}, monotonously grows with increasing

TABLE III

Intensities in the band maxima (I) and band intensity ratios of the thermal degradation of poly-amides. Assignment: $I_{\sim 724}$ methylene group rocking vibration, $I_{\sim 909}$ vinyl group band, $I_{\sim 941}$ Amide IV band of the crystalline phase of the polymer, $I_{\sim 966}$ *trans*-vinylene group, $I_{\sim 1126}$ composite vibration of backbone carbon atoms and methylene groups in the amorphous phase of the polymer, $I_{\sim 1462}$ methylene group bending vibration, $I_{\sim 1544}$ Amide II band, $I_{\sim 2244}$ nitrile group band. For the individual polyamides, the measured values of the corresponding band maxima are given

Heating		I_{724}	I_{909}	I_{966}	I_{1544}	I_{2244}	$\dfrac{I_{1544}}{I_{1544}}$	$\dfrac{I_{1462}}{I_{1544}}$	$\dfrac{I_{941}}{I_{1126}}$	$\dfrac{I_{966}}{I_{1544}}$
C	h			$.10^3$						
PA-12: I_{721}, I_{909}, I_{943}, I_{966}, I_{1120}, I_{1460}, I_{1554}, I_{2244}									
—	—	248	0	0	749	0	0	0·610	0·517	0
300	1	217	0	0	741	0	0	0·637	0·538	0
400	0·5	214	0	0	739	0	0	0·650	0·590	0
400	1	211	10	0	690	18	0·026	0·689	0·533	0
400	2	208	12	5	671	20	0·030	0·697	0·438	0·007
400	4	191	14	9	546	23	0·040	0·717	0·365	0·016
500	0·5	131	58	18	462	62	0·134	1·249	—	0·039
500	1	124	27	29	399	56	0·140	1·548	—	0·073
500	2	108	21	26	323	51	0·158	2·486	—	0·080
500	4	85	15	13	135	41	0·304	2·769	—	0·096
600	1	0	0	0	0	0	—	—	—	—
PA-11: I_{721}, I_{909}, I_{937}, I_{966}, I_{1122}, I_{1461}, I_{1546}, I_{2244}									
—	—	229	0	0	887	0	0	0·556	0·640	0
300	1	191	0	0	748	0	0	0·607	0·642	0
350	0·5	151	9	18	503	31	0·062	0·634	0·500	0·036
350	1	145	87	47	424	103	0·243	1·184	0·372	0·111
350	2	105	20	36	315	98	0·311	1·257	0·080	0·114
350	4	70	8	21	150	63	0·420	2·392	—	0·140
400	0·5	132	66	72	311	118	0·379	1·382	0·155	0·232
400	1	123	84	117	172	176	1·023	2·499	0·148	0·680
400	2	90	49	80	50	105	2·100	4·201	—	1·600
400	4	70	21	58	0	83	—	—	—	—
500	0·5	87	91	138	0	189	—	—	—	—
500	1	74	75	78	0	125	—	—	—	—
500	2	60	45	35	0	68	—	—	—	—
500	4	50	30	44	0	56	—	—	—	—
600	1	0	0	0	0	0	—	—	—	—

TABLE III
(Continued)

°C	h	I_{7a_4}	I_{909}	I_{966} .10^3	I_{1544}	I_{2244}	$\dfrac{I_{2244}}{I_{1544}}$	$\dfrac{I_{1462}}{I_{1544}}$	$\dfrac{I_{941}}{I_{1126}}$	$\dfrac{I_{966}}{I_{1544}}$
PA-8: $I_{724}, I_{909}, I_{941}, I_{965}, I_{1120}, I_{1463}, I_{1545}, I_{2244}$
—	—	228	0	0	1 084	0	0	0·510	0·617	0
270	1	214	0	0	910	0	0	0·516	0·645	0
300	1	212	12	0	880	34	0·039	0·520	0·602	0
350	0·5	151	13	14	804	47	0·058	0·565	0·587	0·017
350	1	99	10	11	597	49	0·082	0·734	—	0·018
350	2	87	8	9	456	51	0·112	0·858	—	0·020
350	4	36	7	6	200	22	0·110	1·412	—	0·030
400	0·5	55	54	16	323	66	0·204	0·954	—	0·050
400	1	50	27	14	236	41	0·174	1·204	—	0·059
400	1·5	44	11	9	111	12	0·108	1·309	—	—
400	2	42	8	8	0	11	—	—	—	—
400	4	40	6	7	0	9	—	—	—	—
500	1	0	0	0	0	0	—	—	—	—
PA-6,6: $I_{727}, I_{909}, I_{934}, I_{965}, I_{1139}, I_{1461}, I_{1535}, I_{2244}$
—	—	164	0	0	960	0	0	0·427	1·210	0
300	1	154	0	0	866	0	0	0·486	1·749	0
350	0·5	117	6	0	786	7	0·009	0·514	2·317	0
350	1	112	10	0	618	12	0·019	0·561	1·932	0
350	2	91	12	0	440	14	0·032	0·577	1·767	0
350	4	74	15	7	178	19	0·107	1·379	—	0·039
400	0·5	40	19	6	317	17	0·053	0·928	—	0·019
400	1	30	15	5	270	13	0·048	0·947	—	0·019
400	1·5	11	5	2	104	5	0·048	1·278	—	0·019
400	2	0	3	1	0	4	—	—	—	—
400	4	0	0	0	0	0	—	—	—	—
500	1	0	0	0	0	0	—	—	—	—

temperature and time of heating. This is caused by the considerable reduction of the Amide II band intensity.

After degradation at 600°C, the surface of the reaction vessel remained covered with a thin, carbonaceous product with metallic lustre, exhibiting no characteristic IR bands (Fig. 2a).

Similarly as in the case of PA-6 degradation products, the IR spectrum of the condensates of PA-12 after degradation was compared with the spectrum of the

monomer, i.e. 12-dodecanelactam. However, in the degradation products of poly-
amide-12, no absorption bands assignable to 12-dodecanelactam could be detected.
This indicates random character of degradation at any amide group in the chain,
without appreciable depolymerization at the chain ends of the macromolecule.

Polyamide-11 (PA-11)

Rilsan BMN G8T was thermally degraded at 300 and 600°C for one hour, and at
350, 400 and 500°C for 0·5, 1, 2 and 4 h (Fig. 2*b*, Table III).

After one hour at 300°C, the IR spectrum of PA-11 exhibits hardly any change.
A slight intensity reduction of the Amide II band at $1\ 546\ \mathrm{cm}^{-1}$ and of the rocking
vibration band of methylene groups at $721\ \mathrm{cm}^{-1}$ indicates loss of amide groups
and splitting of the polymer chain (Table III). In analogy with ref.[11] we have assigned
the Amide IV band at $937\ \mathrm{cm}^{-1}$ to the respective vibration of the polymer in the
crystalline phase, and the band at $1\ 122\ \mathrm{cm}^{-1}$ to the stretching vibration of the
polymer backbone in the amorphous phase. The intensity ratio I_{937}/I_{1122} exhibited
practically no change, i.e. the crystallinity degree remained roughly constant after
one hour of heating at 300°C.

After degradation at 350°C the IR spectrum of polyamide-11 exhibits new bands
at 909, 966, 991 and $2\ 244\ \mathrm{cm}^{-1}$ (Fig. 2*b*). The bands at 909 and $991\ \mathrm{cm}^{-1}$ cor-
respond to vinyl group vibrations[14], the band at $966\ \mathrm{cm}^{-1}$ is assigned to a *trans*-
-vinylene group[14], and the band $2\ 244\ \mathrm{cm}^{-1}$ to the stretching vibration of a nitrile
group[14]. With prolonged heating time, intensity reduction is observed for the band
of Amide II at $1\ 546\ \mathrm{cm}^{-1}$, for the methylene group rocking vibration at $721\ \mathrm{cm}^{-1}$
(Table III), as well as for all other bands connected with amide group vibration.
The band of the methylene group bending vibration is shifted towards lower wave-
numbers, from $1\ 465\ \mathrm{cm}^{-1}$ in Rilsan BMN G8T to $1\ 461\ \mathrm{cm}^{-1}$ in the polymer after
4 h of degradation, i.e. it approaches the value characteristic of n-alkanes[14]. The
band intensity ratio I_{937}/I_{1122} characteristic of the crystallinity degree of PA-11 is
decreasing rapidly. At the same time the band intensity ratio of the methylene group
bending vibration and of Amide II, I_{1461}/I_{1546}, is increasing. Similar changes are also
observed for the intensity ratio of the nitrile group and Amide II bands, I_{2244}/I_{1546}.
The bands of the vinyl group at $909\ \mathrm{cm}^{-1}$, *trans*-vinylene group at $966\ \mathrm{cm}^{-1}$ and
of the nitrile group at $2\ 244\ \mathrm{cm}^{-1}$ are most intense after 1 hour of heating, and
decrease gradually during prolonged heating. It may be assumed that after two
hours of degradation, the rate of depletion of these groups in the reaction space due
to the escape of low-molecular compounds exceeds the rate of their formation by
β-C—H hydrogen transfer or by a radical mechanism from the degraded polymer.

After degradation at 500°C the IR spectrum of the product exhibits a band at
$1\ 637\ \mathrm{cm}^{-1}$ corresponding to a vinyl group vibration[14]. This weak vinyl group band
cannot be observed in IR spectra of degraded PA-11 at lower temperatures, because

it is overlapped by a strong Amide I band. Bands characteristic of polyamides are no longer apparent in the IR spectrum (Fig. 2b). With prolonged heating time, the band intensities of the methylene group rocking vibration at 721 cm^{-1}, of the vinyl group at 909 cm^{-1}, of the *trans*-vinylene group at 966 cm^{-1} and of the nitrile group at $2\,244 \text{ cm}^{-1}$ gradually decrease. The final degradation product of polyamide-11 after one hour at 600°C is a thin layer of carbon with metallic lustre at the surface of the reaction vessel, without any characteristic IR bands.

The IR spectra of the degradation products of PA-11 were compared with the IR spectra of lactams[16,17]. However, no vibration bands assignable to the monomer could be detected in the degradation products.

Polyamide-8 (PA-8)

Polyamide-8 was thermally treated at 270, 300 and 500°C for one hour, and at 350 and 400°C for 0·5, 1, 2 and 4 h (Fig. 2c, Table III).

After one hour of degradation at 270°C the IR spectrum of PA-8 does not practically exhibit any change. A slight reduction of the intensity of the Amide II band at $1\,545 \text{ cm}^{-1}$ and of the band of the methylene group rocking vibration at 724 cm^{-1} indicates loss of amide groups and splitting of polymer chains (Table III). In analogy with ref.[11] we have assigned the Amide IV band at 941 cm^{-1} to the respective vibration of the polymer in the crystalline phase, and the band at $1\,120 \text{ cm}^{-1}$ to the stretching vibration of the polymer backbone in the amorphous phase. An increase of the intensity ratio $I_{941}/_{1120}$ indicates some increase in polymer crystallinity due to melting.

After one hour of thermal degradation at 300°C, a new band appears at $2\,244 \text{ cm}^{-1}$, corresponding to a nitrile group vibration, while the band intensities of amide group vibrations, and also of the methylene group rocking vibration at 724 cm^{-1} undergo further lowering. The band intensity of the composite vibration at $1\,240 \text{ cm}^{-1}$, consisting of the Amide III vibration and of wagging and twisting methylene group vibrations, has been reduced to such an extent that it appears as a shoulder on the band at $1\,255 \text{ cm}^{-1}$ (Fig. 2c, Table III).

After heating at 350°C, in the IR spectrum of PA-8 a band appears at 909 cm^{-1}, corresponding to the vibration of a vinyl group, and at 965 cm^{-1}, assigned to the vibration of a *trans*-vinylene group[14] (Fig. 2c). These two bands exhibit maximum intensity after one half-hour of degradation, later their intensities decay with increasing heating time (Table III). The crystallinity of the polymer, as characterized by the band intensity ratio I_{941}/I_{1120}, rapidly decreases at 350°C. With prolonged heating time, the band intensities of Amide II at $1\,545 \text{ cm}^{-1}$ and of the methylene group rocking vibration at 724 cm^{-1} are rapidly decreasing. The intensity of the nitrile group band at $2\,244 \text{ cm}^{-1}$ increases, reaching a maximum after two hours of degradation, and decreases later on. When the temperature is increased to 400°C,

a new band appears at 748 cm^{-1}, assigned to short carbon chains[15], and in the range of methyl and methylene group stretching vibrations a new band becomes apparent at 2 950 cm^{-1}, assigned to a methyl group stretching vibration[14]. On prolonging the degradation time, rapid destruction of polymer chains occurs, as manifested by the decay of the Amide II band intensity at 1 545 cm^{-1}. The bands of double bonds at 909 and 965 cm^{-1} reach their maximum intensity after one half-hour of degradation, later on their intensity rapidly decreases. The nitrile group band at 2 244 cm^{-1} behaves similarly. This loss of double bonds and nitrile groups in degradation products of polyamide-8 at prolonged thermal treatment is caused by the formation of gaseous products which do not return to the reaction space.

After one hour of degradation at 500°C, no analyzable residue was left from PA-8.

The IR spectra of the degradation products of PA-8 were compared with the IR spectra of lactams[16,17]. However, no vibrational bands of the monomer could be detected in the degradation products.

Polyamide-6,6 (PA-6,6)

PA-6,6 was thermally degraded at 300 and 500°C for one hour, and at 350 and 400°C for 0·5, 1, 2 and 4 h (Fig. 2*d*, Table III).

After one hour of degradation at 300°C, the IR spectrum of PA-6,6 does not exhibit any major change. A slight lowering of the band intensities of Amide II at 1 535 cm^{-1} and of the methylene group rocking vibration at 727cm^{-1} indicates loss of amide groups and splitting of the polymer chain (Table III). An increase of the intensity ratio of the Amide IV band of the crystalline phase at 934 cm^{-1} and of the backbone stretching vibration of the amorphous phase at 1 139 cm^{-1}, I_{934}/I_{1139}, indicates an increase in polymer crystallinity (Table III) due to melting, in agreement with the results of ref.[11].

After degradation at 350°C, the IR spectrum of PA-6,6 exhibits new bands at 909, 965 and 2 244 cm^{-1} (Table III, Fig. 2*d*). The band at 909 cm^{-1} corresponds to a vinyl group vibration[14], the band at 965 cm^{-1} to the vibration of a *trans*-vinylene group[14], and the band at 2 244 cm^{-1} is assigned to the stretching vibration of a nitrile group. With increasing degradation time, the band intensities of double bonds at 909 and 965 cm^{-1} are gradually increasing. The intensity ratio $I_{934}/_{1139}$ used to characterize the crystallinity degree of PA-6,6 reaches its maximum value after one half-hour of degradation at 400°C and decreases later on, indicating that after short heating, recrystallization occurs on subsequent cooling, whereas after prolonged heating, chain degradation takes place, leading to the formation of predominantly amorphous polyamide after cooling.

After heating at 400°C, on the band of the methylene groups in the range of C—H stretching vibrations, a shoulder appears at 2 950 cm^{-1}, assigned to a methyl group vibration[14]. With prolonged degradation time at 400°C, the band intensities of

Amide II at $1\ 535\ cm^{-1}$ are decreasing. The bands of the vinyl and *trans*-vinylene groups at 909 and $965\ cm^{-1}$ exhibit maximum intensity after one half-hour of degradation, later on their intensity is decreasing. The nitrile group band at $2\ 244\ cm^{-1}$ behaves similarly (Table III). The lowering of the content of double bonds and nitrile groups in the degradation products of polyamide-6,6 at longer heating times is caused by the generation of gaseous products which do not return to the reaction space.

After one hour of degradation at 500°C, no products from PA-6,6 remained in the reaction space. The reaction vessel contained only short glass fibres introduced by the producer to attain the desired service properties of the polymer (Fig. 2d).

Rate of Polyamide Degradation

Thermal degradation of polyamides may be regarded as a first order decomposition reaction, where the reaction rate at every instant is proportional to the concentration of the reacting substance. As according to the Lambert–Beer law, the intensity of a band maximum is proportional to concentration, the course of the process could be estimated from the dependence of $\ln I$ on degradation time (t). The bands of the generated double bonds or nitrile groups at 910, 966, and $2\ 244\ cm^{-1}$ are not suitable for evaluation of the reaction rate, because these groups may be present in low-molecular degradation products which can escape from the reaction space. On the other hand, plots of $\ln I_{\mathrm{Amide\ II}}$ vs t give a reliable estimate of the degradation process. The rate constants of degradation (k_T) for the temperatures of 350° and 400°C in the series PA-12, PA-11, PA-8, and PA-6,6 could suggest that the stability of the studied polyamides decreases with the decreasing number of carbon atoms between the amide groups in the chain.

Polyamide:	PA-12	PA-11	PA-8	PA-6,6
$k_{350} . 10^3$, min^{-1}:	—	5·751	6·440	6·960
$k_{400} . 10^3$, min^{-1}:	1·381	20·352	—	—

The found values for k_T of PA-6,6, PA-8, and PA-11 are roughly equal, and differ considerably from k_T of PA-12. However, the behaviour of the polymers during heating could be affected by fillers, stabilizers etc. For PA-8 and PA-6,6 at 400°C, the respective plots indicate that the formation of high amounts of low-molecular gaseous products which escape from the reaction spaec causes an apparent enhancement of the content of amide groups in the remaining condensate and distorts the results. A similar behaviour is observed with PA-12 after 2 h of degradation at 500°C.

From the graphical dependence of $\ln I_{\mathrm{Amide\ II}}$ on t for PA-6 at 400°C it is evident that at prolonged degradation times, the intensity in the maximum of the Amide II

band approaches a limiting value, indicating the establishment of a dynamical equilibrium between PA-6 and ε-caprolactam under the given conditions. At 500°C destruction of polyamide-6 is so deep that upon cooling after 4 h of degradation, a considerable part of the decomposed PA-6 remains in the form of ε-caprolactam dimer.

CONCLUSION

The data obtained from IR spectra of condensates of degraded polyamides indicate

a) With PA-6, PA-6,6, PA-8 and PA-12 at temperatures about 300°C, crystallinity is increasing due to melting. Further temperature enhancement and prolongation of heating time leads to the destruction of macromolecules and formation of predominantly amorphous or liquid degradation products.

b) In the IR spectra of the degradation products of the studied polyamides there appear bands of vinyl and nitrile end groups which permit us to postulate a possible decomposition mechanism of the amide groups in the polymer by β-C—H hydrogen transfer. At higher temperatures, however, the concentration of these end groups decreases. This is probably caused by a rapid escape of low-molecular gaseous products containing these groups.

c) The monotonously increasing ratio of the intensities in the band maxima of the *trans*-vinylene group and the Amide II vibrations is in agreement with the notion that at temperatures over 300°C, the polyamides are also degraded by a radical mechanism, the contribution of which grows with increasing temperature and prolonged heating time.

d) The stability of polyamides during heating in inert atmosphere decreases in the series PA-12 ≫ PA-11 ≧ PA-8 ≧ PA-6,6.

e) With all the studied polyamides, the composition of the degradated condensed products depends on temperature and time. By prolonging the heating time at lower temperature it is not possible to obtain degradation products of similar composition as by degradation at a higher temperature. By comparing the intensities in the maxima of selected bands, and the band intensity ratios of a studied sample, it is possible to estimate both the temperature and the duration of heating which the polyamide had undergone.

REFERENCES

1. Achhammer B. G., Reinhart F. W., Kline G. M.: J. Appl. Chem. *4*, 301 (1951).
2. Achhammer B. G., Reinhart F. W., Kline G. M.: J. Res. Natl. Bur. Stand.(U.S.) *46*, 391, (1951).
3. Straus S., Wall L.: J. Res. Natl. Bur. Stand. (U.S.) *60*, 39 (1958).
4. Straus S., Wall L.: J. Res., A *63*, 269 (1959).

5. Conway D. C., Marak R.: J. Polym. Sci., Polym. Chem. Ed. *20*, 1765 (1982).
6. Ballistreli A., Garozzo D., Giuffrida M., Montaudo G.: Macromolecules *20*, 2991 (1987).
7. Katorzhnov N. D., Strepikheyev A. S.: Zh. Prikl. Khim. (Leningrad) *32*, 625 (1959).
8. Katorznov N. D., Strepikheyev A. S.: Zh. Prikl. Knim. (Leningrad) *32*, 363 (1959).
9. Smith S.: J. Polym. Sci. *30*, 459 (1958).
10. Luderwald L., Merz F.: Angew. Makromol. Chem. *74*, 165 (1978).
11. Do C. H., Pearce E. M., Bulkin B. J., Reimschussel H. K.: J. Polym. Sci., Polym. Chem. Ed. *25*, 2409 (1987).
12. Svoboda M., Schneider B., Štokr J.: Collect. Czech. Chem. Commun. *55*, 2233 (1990).
13. Dechant J., Danz R., Kimmer W., Schmolke R.: *Infrared Spectroscopy of Polymers*. Khimiya, Moscow 1976.
14. Horák M., Papoušek D.: *Infračervená spektra a struktura molekul*. Academia, Praha 1976.
15. Hummel O. D.: *Atlas der Kunststoff-Analyse*. Carl Hanser Verlag, München 1968.
16. Chen C. Y., Swenson C. A.: J. Phys. Chem. *73*, 1363 (1969).
17. Chen C. Y., Swenson C. A.: J. Phys. Chem. *73*, 2999 (1969).

Translated by D. Doskočilová.