Thermal decomposition processes in polyhydrazides and polyoxamides investigated by mass spectrometry

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The thermal decomposition processes of some totally aromatic or totally aliphatic polyhydrazides and polyoxamides were studied by direct pyrolysis mass spectrometry, using both chemical ionization and electron impact modes. The results indicate that the primary thermal decomposition processes of these polymers (containing -CO-CO- and -NR-NR- linkages) are strongly influenced by structural factors. The polyhydrazide I, derived from isophthalic acid and hydrazine, experiences primary loss of water, producing a polymer with oxadiazole units. The latter thermally decomposes with formation of compounds with nitrile, phenyl, amino and/or acid end groups. The thermal decomposition of the polyhydrazide II, derived from isophthalic acid and *N,N'*-dimethylhydrazine, proceeds via an α C-H hydrogen transfer process from methyl groups, with formation of pyrolysis products containing secondary amide and/or imine end groups. Hydrolysis of the latter groups leads to the formation of primary amide end groups and subsequent formation of nitrile end groups. The primary thermal decomposition process of the polyhydrazide III, derived from adipic acid and hydrazine, proceeds via a C-H hydrogen transfer to the nitrogen atom, with formation of compounds with amine and/or cyclopentanone end groups. In the pyrolysis of this polyhydrazide, secondary thermal fragments are also formed: cyclopentanone, carbon dioxide and compounds with azomethine and isocyanate groups. The polyoxamide IV, derived from oxalic acid and *m*-phenylenediamine, decomposes via a N-H hydrogen transfer process with formation of compounds with amine and/or isocyanate end groups. Finally, the thermal degradation of the polyoxamide V, derived from oxalic acid and ethylenediamine, proceeds via a β C-H hydrogen transfer process, with formation of compounds with olefin and amide end groups.

(Keywords: polyhydrazides; polyoxamides; thermal degradation; chemical ionization mass spectrometry)

INTRODUCTION

The characterization of polymers by direct pyrolysis mass spectrometry (DPMS) yields important structural information[1-3]. Typical applications of this method include: structural identification of homopolymers, differentiation of isomeric structures, copolymer composition and sequential analysis, identification of oligomers formed in the polymerization reactions and identification of volatile additives contained in polymer samples[1-3].

In the DPMS technique[1-3], polymers are introduced via the direct insertion probe and the temperature is increased gradually up to a point at which thermal degradation reactions occur; the volatile oligomers formed are then ionized and detected. The mass spectrum of a polymer obtained in these conditions is therefore that of the mixture of oligomers formed by pyrolysis.

A general advantage of this technique is that pyrolysis is accomplished under high vacuum, and therefore the thermal oligomers formed are volatilized and removed readily from the hot zone. This, together with the low probability of molecular collision and fast detection, reduces to a great extent the occurrence of secondary reactions, so that almost exclusively primary fragments are detected. Consequently, the information thus obtained is of particular importance in order to assess the primary thermal degradation mechanism of a polymer. Furthermore, since pyrolysis is achieved very close to the ion source and no problem of transport exists, fragments of high mass, which are often essential for the structural characterization of the polymer, can be detected, whereas they are often lost using other techniques.

The main problem connected with this technique is, however, the identification of the products in the spectrum of the multicomponent mixture produced by thermal degradation. In fact, in the overall end spectrum of a polymer, the molecular ions of the thermal oligomers will appear mixed with the fragment ions formed in the ionizing step. In some instances, identification of thermal degradation products can be achieved by using soft ionization methods and exact mass measurements and by

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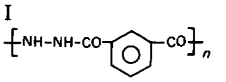
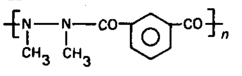
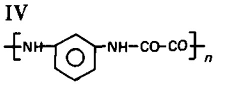
Table 1 Structure, thermal stability, residue and viscosity of the polymers investigated

Polymer	PDT^a (°C)		R^b (%)	η_{inh}^c
	Pure sample	Mixture with Na benzoate		
I 	345; 485	–	49.5	0.22^d
II 	430	385	8.5	0.12^d
III $\left[\text{NH-NH-CO}\left(CH_2\right)_4\text{CO}\right]_n$	360	–	28.0	0.16^d
IV 	415	400	30.0	0.11^e
V $\left[\text{NH}\left(CH_2\right)_2\text{NH-CO-CO}\right]_n$	460	350	6.0	0.10^e

[a] Temperature of maximum decomposition rate of the polymer
[b] Residue taken at 800°C, from thermogravimetric experiments under nitrogen atmosphere
[c] $\eta_{inh} = \ln \eta_r/c$; $c = 0.5$ g dl^{-1}
[d] In DMF + LiCl (3 wt%) at 30±0.02°C
[e] In H_2SO_4 at 40±0.02°C

matching spectra of authentic samples with those obtained from the polymer[1-9].

In previous studies[1,3-9] we have investigated several classes of polymers by DPMS methods. Here we report a similar study for some totally aromatic and totally aliphatic polyhydrazides and polyoxamides (*Table 1*).

Various aspects of the chemistry and properties of these polymers have been investigated[10-24]. In the case of polyhydrazides[10-18], interest has been directed to the thermal behaviour[10,11], to the formation of high-modulus wholly aromatic fibres[12,13] and to the study of rheological properties[14-17]. In the last few years interest has also been directed to the synthesis of polymers for reverse osmosis membranes[18]. Also, in the case of polyoxamides, the studies have focused on synthesis and characterization[19-24]. To our knowledge, the thermal degradation processes of the polyhydrazides and polyoxamides have not been investigated.

The results of the present study indicate that the primary thermal decomposition processes of these polymers (containing –CO–CO– and –NR–NR– linkages) are strongly influenced by structural factors.

The aromatic polyhydrazide I (*Table 1*), derived from isophthalic acid and hydrazine, experiences primary loss of water, producing a polymer with oxadiazole units[10-16]. The latter thermally decomposes with formation of compounds with nitrile, phenyl, amino and/or acid end groups.

The thermal decomposition of the aromatic polyhydrazide II (*Table 1*) (which cannot lose water because of the *N*-methyl substitution), derived from isophthalic acid and *N*,*N*′-dimethylhydrazine, proceeds via a α C–H hydrogen transfer process from methyl groups, with formation of pyrolysis products containing secondary amide and/or imine end groups. Hydrolysis of the latter groups leads to the formation of primary amide end groups and subsequent formation of nitrile end groups.

The primary thermal decomposition process of the aliphatic polyhydrazide III (*Table 1*), derived from adipic acid and hydrazine, is very different from the two aromatic polyhydrazides I and II. It proceeds via a C–H hydrogen transfer to the nitrogen atom, with formation of compounds with amine and/or cyclopentanone end groups. In the pyrolysis of this polyhydrazide, secondary thermal fragments are also formed: cyclopentanone, carbon dioxide and compounds with azomethine and isocyanate groups.

The aromatic polyoxamide IV (*Table 1*), derived from oxalic acid and *m*-phenylenediamine, decomposes via a N–H hydrogen transfer process with formation of compounds with amine and/or isocyanate end groups.

Finally, the thermal degradation of the aliphatic polyoxamide V (*Table 1*), derived from oxalic acid and ethylenediamine, proceeds via a β C–H hydrogen transfer process, with formation of compounds with olefin and amide end groups.

EXPERIMENTAL

Materials

Adipoyl chloride was prepared and purified by standard techniques from adipic acid and thionyl chloride.

Other basic materials, i.e. hydrazine, *N*,*N*′-dimethylhydrazine, isophthaloyl dichloride, *m*-phenylenediamine, oxalyl dichloride and diethyl oxalate, were commercial products appropriately purified before use.

Polymerization

Polymerizations were carried out by different methods. Here we report only those methods which yielded the highest viscosities. Polyhydrazide I was synthesized by dispersion polycondensation[25], polyhydrazides II and III and polyoxamide IV were prepared by interfacial polycondensation, whereas polyoxamide V was synthesized by solution polycondensation.

Polymer I. In a typical dispersion polycondensation procedure (polyhydrazide I, *Table 1*), in the container of a Waring blender, precooled in a refrigerator, were placed 6.36 g (0.06 mol) of sodium carbonate in 40 ml of water and 1.50 g (0.03 mol) of hydrazine hydrate in 10 ml of water. To the rapidly stirred system was added in one application 6.09 g (0.03 mol) of isophthaloyl dichloride in 46 ml of tetrahydrofuran (THF). The mixture was stirred for 5 min and then poured into an excess of cold water. THF was removed by gentle warming under vacuum and the polymer that precipitated was filtered, washed with water and methyl alcohol, and dried *in vacuo* at 60°C for 24 h. Yield: 100%.

Polymers II, III and IV. In a typical interfacial polycondensation procedure (polyhydrazide II, *Table 1*), in the container of a Waring blender, precooled in a refrigerator, were placed under stirring 6.09 g (0.03 mol) of isophthaloyl dichloride dissolved in 46 ml of dichloromethane, 3.99 g (0.03 mol) of *N,N′*-dimethylhydrazine dihydrochloride and 12.72 g (0.12 mol) of sodium carbonate in 50 ml of water, in one application. The mixture was stirred for 5 min and then poured into an excess of cold water. Dichloromethane was removed in a rotary evaporator and the polymer that precipitated was filtered, washed with water and methyl alcohol, and dried *in vacuo* at 60°C for 24 h. Yield: 75%.

Polymer V. In this case, a solution polymerization (instead of an interfacial one) was used in order to increase the yield of the polymer. In a one-necked flask were placed 1.17 g (0.015 mol) of ethylenediamine hydrate and 2.19 g (0.015 mol) of diethyl oxalate in 100 ml of toluene. To remove the water contained in the diamine, a Markusson apparatus was connected to the flask. The reaction mixture was heated and stirred for 2 h. Toluene was then removed in a rotary evaporator and the polymer that precipitated was filtered, washed with toluene and methyl alcohol, and dried *in vacuo* at 60°C for 24 h. Yield: 80%.

Viscometry

Inherent viscosities ($\eta_{\text{inh}} = \ln \eta_r / c$; $c = 0.5\ \text{g dl}^{-1}$) were measured in a Desreux–Bishoff suspended-level viscometer which contained a coarse sintered glass filter attached just below the reservoir through which the solutions passed as they rose into the capillary. The temperatures and the solvents used are listed in *Table 1*.

Thermogravimetry

Thermal analyses were performed with a Perkin–Elmer TGS/2 apparatus in a nitrogen atmosphere (60 ml min^{-1}) at a heating rate of 10°C min^{-1}. Polymer decomposition temperatures (*PDT*) of the investigated polyhydrazides and polyoxamides, as indicated by the maxima in their differential thermogravimetric curves, are listed in *Table 1*.

Mass spectrometry

A double-focusing Kratos MS 50 S equipped with the standard electron impact or chemical ionization sources and a DS 55 data system was used to obtain mass spectra. The instrument was scanned from $m/z = 1000$ to $m/z = 20$, with a scan rate of 10 s/decade. Perfluorokerosene (PFK) was used for computer calibration; the ion source was maintained at 200°C.

Positive chemical ionization (CI) mass spectra were obtained with isobutane as reagent gas. Isobutane (99.5%) was purchased from Matheson Gas products.

Polymers were pyrolysed directly in the ion source using standard Kratos probes, heated from 30 to 400°C at a heating rate of 10°C min^{-1}.

Electron impact (EI) mass spectra of polyhydrazide I were obtained on a LKB-9000 S mass spectrometer; the heating rate was about 10°C min^{-1} from 30 to 480°C.

RESULTS

Thermal stability

The thermal stabilities of the polymers investigated, indicated by the maxima in their differential thermogravimetric curves (polymer decomposition temperatures, *PDT*), are reported in *Table 1*. Temperatures of maximum volatilization rate, observed on the mass spectrometer by monitoring the total ion current (*TIC*) for polymers in *Table 1*, match quite well those recorded by thermogravimetry.

In our investigation it was observed that, similarly to other polyamides[8,26], the addition of Na salts of simple carboxylic acids is capable of lowering the *PDT* of the polyhydrazides and polyoxamides in *Table 1*. This effect is well known[3,8,26], and we have ascertained that the pyrolysis products obtained in the presence of sodium benzoate are unchanged with respect to the pyrolysis of the pure polymer. The addition of sodium benzoate has therefore been utilized to obtain CI mass spectra of polymers at temperatures of about 350–400°C.

Direct pyrolysis mass spectrometry

Polyhydrazide I. The weight loss curve of polyhydrazide I against temperature is reported in *Figure 1a*. The first thermal reaction occurs at temperatures ranging from 320 to 360°C. The weight loss is about 11.5% and, as already known[10–16], it corresponds to the quantitative loss of water with formation of a polymer having oxadiazole units along the chain (*Scheme Ia*). Mass spectra taken in this temperature range exhibit only one abundant peak corresponding to the molecular ion of water. The second decomposition step (*Figure 1a*) occurs

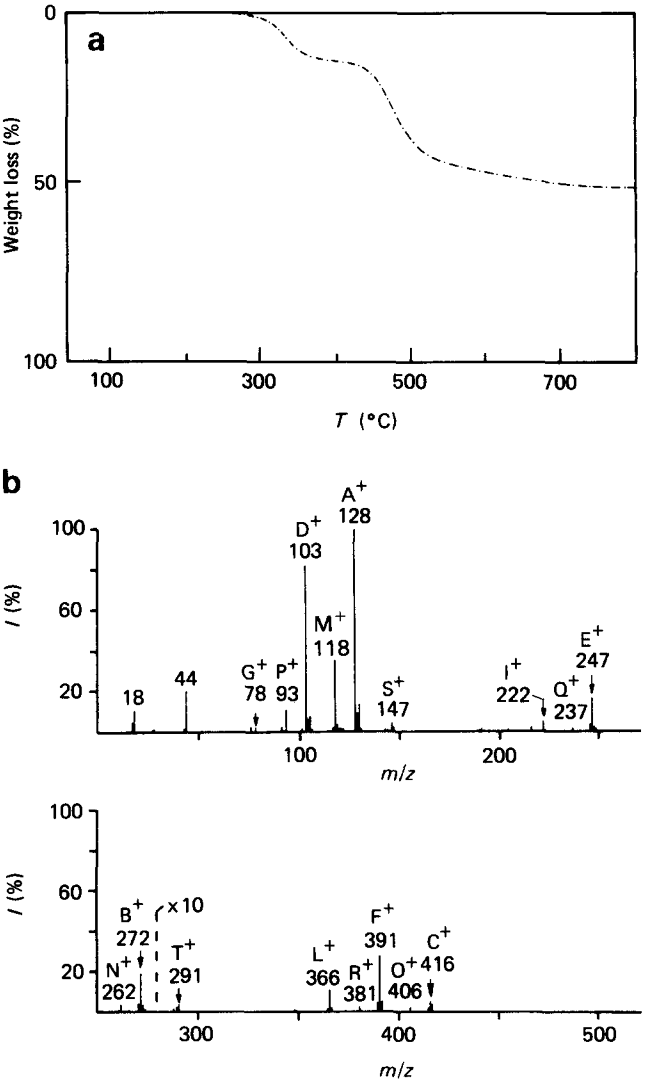
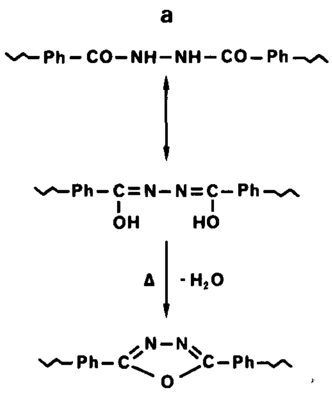
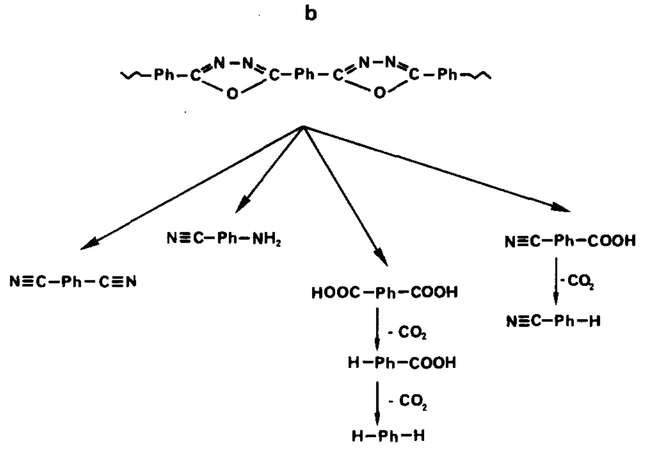


Figure 1 (a) Thermogravimetric curve of polyhydrazide I under nitrogen atmosphere (60 ml min^{-1}); heating rate 10°C min^{-1}. (b) EI mass spectrum (18 eV) of the products of thermal degradation of polyhydrazide I at 480°C

Scheme Ia

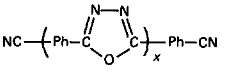
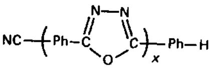
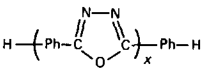
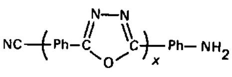
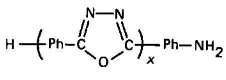
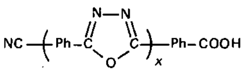
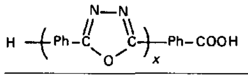


Scheme Ib



Scheme I Thermal decomposition processes for polyhydrazide I at (a) 345°C and (b) 485°C

Table 2 Thermal products formed in the thermal degradation of polyhydrazide I

Thermal product	Symbol		m/z
	A^+	$x=0$	128
	B^+	$x=1$	272
	C^+	$x=2$	416
	D^+	$x=0$	103
	E^+	$x=1$	247
	F^+	$x=2$	391
	G^+	$x=0$	78
	I^+	$x=1$	222
	L^+	$x=2$	366
	M^+	$x=0$	118
	N^+	$x=1$	262
	O^+	$x=2$	406
	P^+	$x=0$	93
	Q^+	$x=1$	237
	R^+	$x=2$	381
	S^+	$x=0$	147
	T^+	$x=1$	291
	U^+	$x=0$	122
	V^+	$x=1$	266

at temperatures ranging from 440 to 510°C. The residue at 800°C is about 50% of the original weight, based on dry polymer.

The EI mass spectrum of polyhydrazide I, recorded at 18 eV and obtained at a probe temperature of 480°C, is reported in *Figure 1b*. A series of intense peaks due to molecular ions of pyrolysis products appear in the EI mass spectrum, and their structures are assigned in *Table 2*. Molecular ions of compounds with dinitrile end groups ($m/z = 128$, base peak; $m/z = 272$ and 416), with nitrile and phenyl end groups ($m/z = 103$, 247 and 391), with diphenyl end groups ($m/z = 78$, 222 and 366), with nitrile and amine end groups ($m/z = 118$, 262 and 406) and with phenyl and amine end groups ($m/z = 93$, 237, 381) are distinguishable (*Table 2*).

In the EI mass spectrum are also present, with low intensity, peaks corresponding to molecular ions of thermal compounds with nitrile and carboxylic acid end groups ($m/z = 147$ and 291) and with phenyl and carboxylic acid end groups ($m/z = 122$ and 266) (*Table 2*). The latter compounds, because of the high temperature of polymer decomposition, show a very high tendency to lose carbon dioxide ($m/z = 44$), present in the EI mass spectrum in *Figure 1b*. Low quantities of water are present in the mass spectrum in *Figure 1b* ($m/z = 18$), presumably coming from the pyrolysis of oxadiazole units.

Polyhydrazide II. The isobutane CI mass spectrum of polyhydrazide II, recorded at a probe temperature of 385°C, is shown in *Figure 2*. In this mass spectrum almost all peaks correspond to protonated molecular ions of primary or secondary thermal products; their structures are assigned in *Table 3*. The most important peaks correspond to protonated molecular ions of compounds with secondary amide end groups ($m/z = 193$, base peak; and $m/z = 383$), with secondary amide and imine end groups ($m/z = 191$ and 381), with secondary and primary amide end groups ($m/z = 179$ and 369) and with secondary amide and nitrile end groups ($m/z = 161$ and 351). Other peaks, corresponding to protonated molecular ions of minor pyrolysis products, are present with low intensity in the CI mass spectrum, and their structures are assigned in *Table 3*.

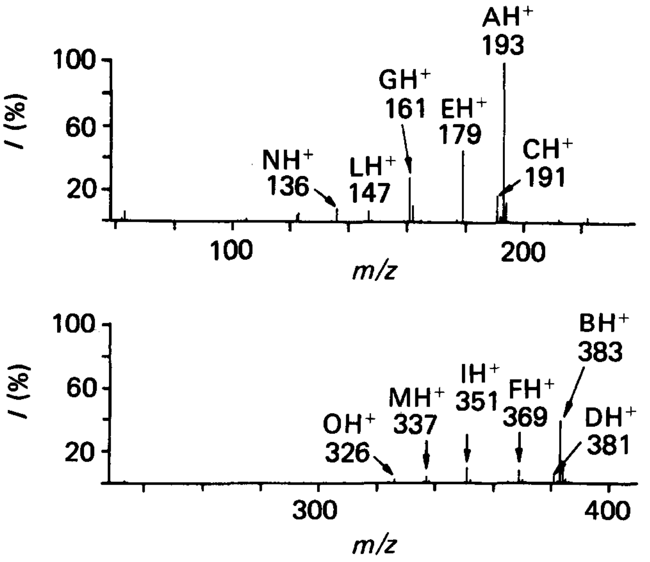
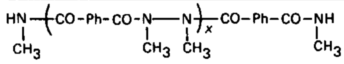
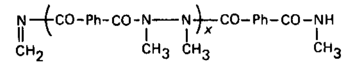
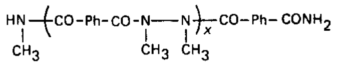
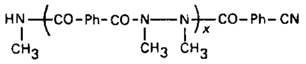
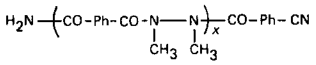
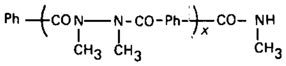


Figure 2 Isobutane CI mass spectrum of the products of thermal degradation of polyhydrazide II at 385°C

Table 3 Thermal products formed in the thermal degradation of polyhydrazide II

Thermal product	Symbol		m/z
 $\mathrm{HN(CH_3)\!-\!(CO\!-\!Ph\!-\!CO\!-\!N(CH_3)\!-\!N(CH_3))_x\!-\!CO\!-\!Ph\!-\!CO\!-\!NH(CH_3)}$	AH^+	$x=0$	193
	BH^+	$x=1$	383
 $\mathrm{N(=CH_2)\!-\!(CO\!-\!Ph\!-\!CO\!-\!N(CH_3)\!-\!N(CH_3))_x\!-\!CO\!-\!Ph\!-\!CO\!-\!NH(CH_3)}$	CH^+	$x=0$	191
	DH^+	$x=1$	381
 $\mathrm{HN(CH_3)\!-\!(CO\!-\!Ph\!-\!CO\!-\!N(CH_3)\!-\!N(CH_3))_x\!-\!CO\!-\!Ph\!-\!CONH_2}$	EH^+	$x=0$	179
	FH^+	$x=1$	369
 $\mathrm{HN(CH_3)\!-\!(CO\!-\!Ph\!-\!CO\!-\!N(CH_3)\!-\!N(CH_3))_x\!-\!CO\!-\!Ph\!-\!CN}$	GH^+	$x=0$	161
	IH^+	$x=1$	351
 $\mathrm{H_2N\!-\!(CO\!-\!Ph\!-\!CO\!-\!N(CH_3)\!-\!N(CH_3))_x\!-\!CO\!-\!Ph\!-\!CN}$	LH^+	$x=0$	147
	MH^+	$x=1$	337
 $\mathrm{Ph\!-\!(CO\,N(CH_3)\!-\!N(CH_3)\!-\!CO\!-\!Ph)_x\!-\!CO\!-\!NH(CH_3)}$	NH^+	$x=0$	136
	OH^+	$x=1$	326

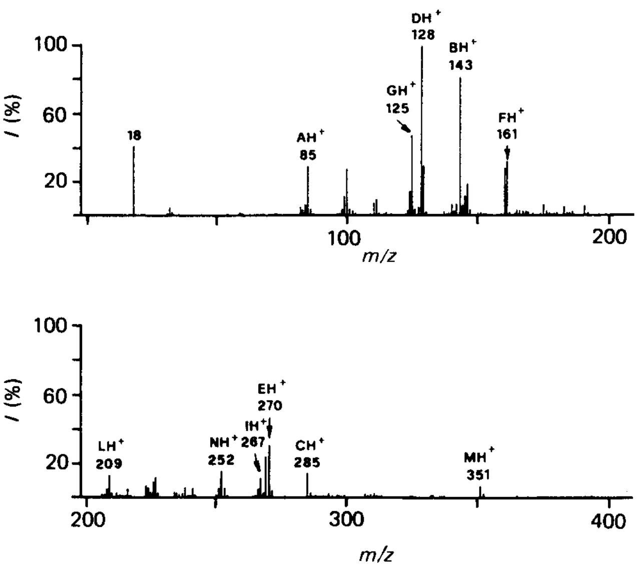
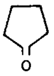
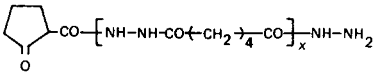
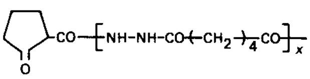
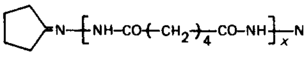
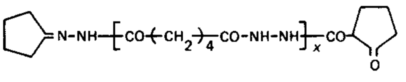
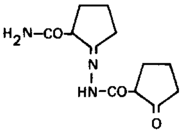


Figure 3 Isobutane CI mass spectrum of the products of thermal degradation of polyhydrazide III at 360°C

Polyhydrazide III. The isobutane CI mass spectrum of polyhydrazide III, recorded at a probe temperature of 360°C, is shown in *Figure 3*. Several intense peaks due to protonated molecular ions of pyrolysis products appear in the CI mass spectrum and their structures are assigned in *Table 4*. One important and diagnostic peak present in the CI mass spectrum is the protonated molecular ion of cyclopentanone ($m/z=85$). Other peaks are distinguishable and they correspond to protonated molecular ions of thermal compounds having cyclopentanone and hydrazine end groups ($m/z=143$ and 285) and cyclopentanone and amide end groups ($m/z=128$, base peak; and $m/z=270$). Another family of thermal compounds having azomethine groups is also present in the CI mass spectrum. These compounds show peaks at $m/z=125$, 209, 252, 267 and 351 (*Table 4*).

Polyoxamide IV. The isobutane CI mass spectrum of polyoxamide IV, recorded at a probe temperature of 400°C, is shown in *Figure 4*. The CI mass spectrum is dominated by a series of peaks at odd mass numbers corresponding to the protonated molecular ions of pyrolysis products. The structures are assigned in *Table 5*. In the CI mass spectrum, peaks corresponding to protonated molecular ions of compounds with diamine end groups ($m/z=109$, base peak; and $m/z=271$) and with amine and isocyanate end groups ($m/z=135$ and 297) are observed. Other low-intensity peaks are present in the mass spectrum and their structures are shown in *Table 5*. Of particular interest is the peak at $m/z=119$, corresponding to the protonated molecular ion of *m*-cyanoaniline.

Table 4 Thermal products formed in the thermal degradation of polyhydrazide III

Thermal product	Symbol		m/z
	AH^+		85
	BH^+	$x=0$	143
	CH^+	$x=1$	285
	DH^+	$x=0$	128
	EH^+	$x=1$	270
$\mathrm{H_2N\!-\!NH\!-\!CO\!-\!(CH_2)_4\!-\!CO\!-\!OH}$	FH^+		161
	GH^+	$x=0$	125
	IH^+	$x=1$	267
	LH^+	$x=0$	209
	MH^+	$x=1$	351
	NH^+		252

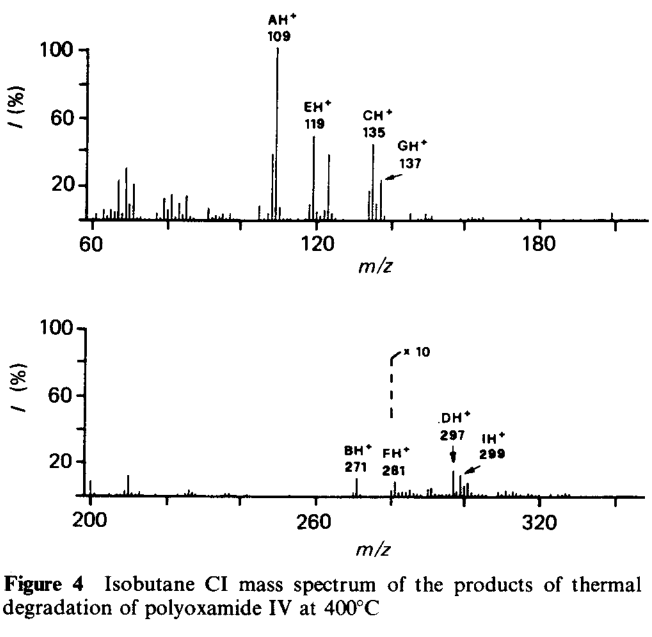


Figure 4 Isobutane CI mass spectrum of the products of thermal degradation of polyoxamide IV at 400°C

Table 5 Thermal products formed in the thermal degradation of polyoxamide IV

Thermal product	Symbol		*m/z*
$H_2N(Ph\text{-}NH\text{-}CO\text{-}CO\text{-}NH)_xPh\text{-}NH_2$	AH^+ BH^+	$x=0$ $x=1$	109 271
$H_2N(Ph\text{-}NH\text{-}CO\text{-}CO\text{-}NH)_xPh\text{-}NCO$	CH^+ DH^+	$x=0$ $x=1$	135 297
$H_2N(Ph\text{-}NH\text{-}CO\text{-}CO\text{-}NH)_xPh\text{-}CN$	EH^+ FH^+	$x=0$ $x=1$	119 281
$H_2N(Ph\text{-}NH\text{-}CO\text{-}CO\text{-}NH)_xPh\text{-}NH\text{-}CHO$	GH^+ IH^+	$x=0$ $x=1$	137 299

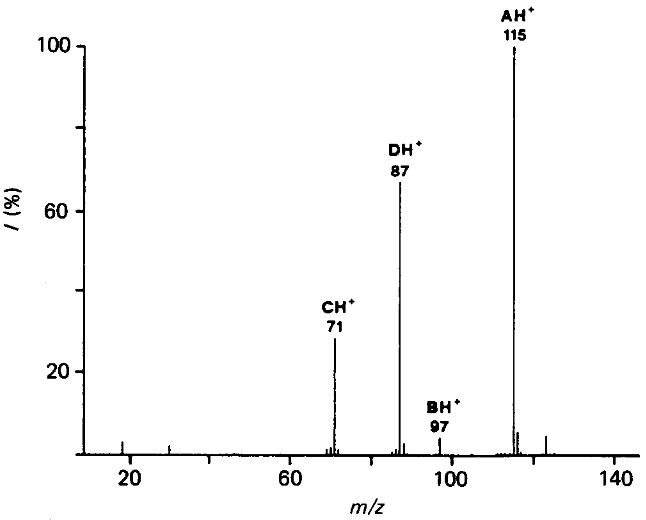


Figure 5 Isobutane CI mass spectrum of the products of thermal degradation of polyoxamide V at 350°C

Polyoxamide V. The isobutane CI mass spectrum of polyoxamide V, recorded at a probe temperature of 350°C, is shown in *Figure 5*. Only four peaks, corresponding to the protonated molecular ions of the pyrolysis products (see below), are present in the CI mass spectrum and their structures are shown in *Table 6*. The base peak of the spectrum ($m/z=115$) is the protonated molecular ion of the compound with amide and olefin end groups (*Table 6*). This compound is very unstable to electron impact and, in fact, it is nearly absent in the EI mass spectrum (omitted for brevity). Two other intense peaks are present in the CI mass spectrum; they correspond to the protonated molecular ions of cyanooxamide ($m/z=71$) and of a compound with amine and isocyanate end groups ($m/z=87$) (*Table 6*). Finally, another peak is present with low intensity at $m/z=97$; it corresponds to the protonated molecular ion of a compound with olefin and nitrile end groups (*Table 6*).

Thermal decomposition processes

The DPMS of polyhydrazides and polyoxamides investigated in the study (*Table 1*) indicates that various types of hydrogen transfer reactions predominate in the thermal decomposition processes of these polymers.

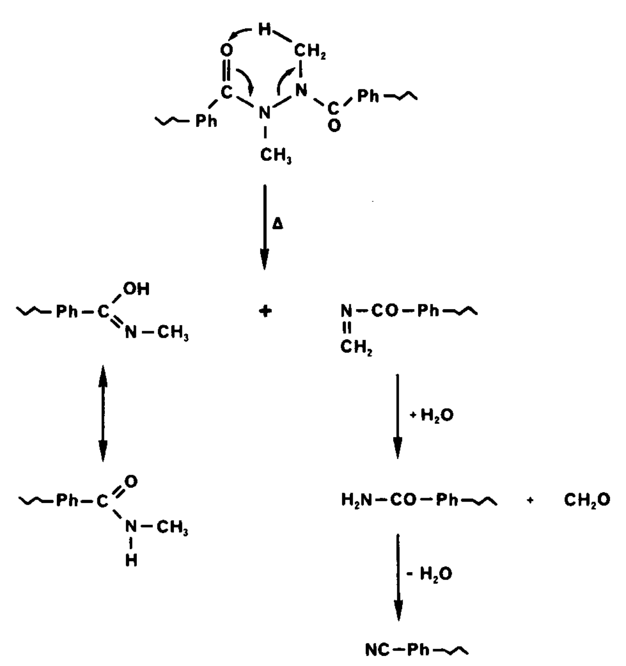
The results obtained in the DPMS analysis of the aromatic polyhydrazide I indicate that the first thermal reaction, i.e. loss of water, leading to the formation of oxadiazole units, occurs through a tautomerization reaction (*Scheme Ia*)$^{10-16}$. The analysis of thermal products generated in the second decomposition step indicates that the pyrolysis occurs through a complex rearrangement of the polymeric chain with formation of several thermal compounds (*Table 2* and *Scheme Ib*). The formation of nitrile groups is strongly favoured at high temperature, as shown by the intense peaks in the CI mass spectrum in *Figure 1b* ($m/z=103$, 118, 128, 247, 272 and 416). It is likely that this process causes the molecular rearrangement, also leading to the other pyrolysis products (*Table 2* and *Scheme Ib*). At the present stage there is not enough information to allow one to sketch a more detailed mechanism for this decomposition.

The results obtained in the DPMS analysis of the *N*-methyl-substituted polyhydrazide II indicate that this polymer decomposes via an α C–H hydrogen transfer process from methyl groups, with formation of pyrolysis products containing amide and/or imine end groups (*Scheme II*). In fact, in the CI mass spectrum in *Figure 2*, intense peaks corresponding to protonated molecular ions of primary thermal compounds are present at $m/z=193$ and 383 (amide end groups) and at $m/z=191$ and 381 (amide and imine end groups), respectively (*Table 3*). Primary pyrolysis products containing imine end groups can undergo hydrolytic reactions^{27} (*Scheme II*), with formation of compounds having primary amide end

Table 6 Thermal products formed in the thermal degradation of polyoxamide V

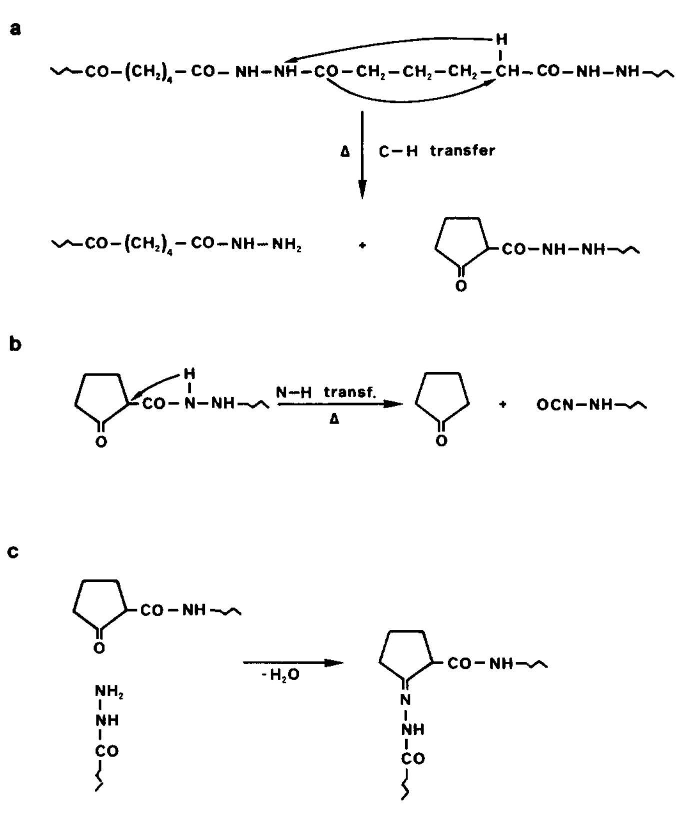
Thermal product	Symbol	*m/z*
$CH_2{=}CH\text{-}NH\text{-}CO\text{-}CO\text{-}NH_2$	AH^+	115
$CH_2{=}CH\text{-}NH\text{-}CO\text{-}CN$	BH^+	97
$H_2N\text{-}CO\text{-}CN$	CH^+	71
$H_2N\text{-}CH_2\text{-}CH_2\text{-}NCO$	DH^+	87

Scheme II



Scheme II Thermal decomposition processes for polyhydrazide II

Scheme III



Scheme III Thermal decomposition processes for polyhydrazide III: (a) primary process; (b) secondary process; (c) further thermal reactions among pyrolysis products

groups (*m*/*z* = 179 and 369, *Figure 2* and *Table 3*). Furthermore, these secondary pyrolysis products can lose water (*Scheme II*), with formation of compounds with nitrile end groups (*m*/*z* = 147, 161, 337 and 351, *Figure 2* and *Table 3*). The presence of secondary and tertiary products indicates that the timescale of the DPMS experiment is too slow in this case to prevent further thermal reactions.

Inspection of the data obtained for the aliphatic polyhydrazide III indicates that this polymer degrades in a different way from the aromatic polyhydrazide I, via a C–H hydrogen transfer to the nitrogen atom, with formation of compounds having hydrazine and cyclopentanone end groups (*Scheme IIIa*). In fact, the CI mass spectrum in *Figure 3* shows several peaks which can be assigned to the above compounds (*Table 4*). These primary thermal products decompose further with formation of secondary thermal fragments by a N–H hydrogen transfer process (*Scheme IIIb*), with formation of cyclopentanone and products with isocyanate end groups (*Figure 3* and *Table 4*). Finally, further thermal reactions occur among the pyrolysis products formed in the thermal decomposition of polyhydrazide III. In *Scheme IIIc* is shown the formation of compounds having azomethine groups. It must be remarked that the reactions shown in *Scheme III* are not uncommon among polymers containing adipic acid units, as we have already observed in the pyrolysis of several polyamides[7].

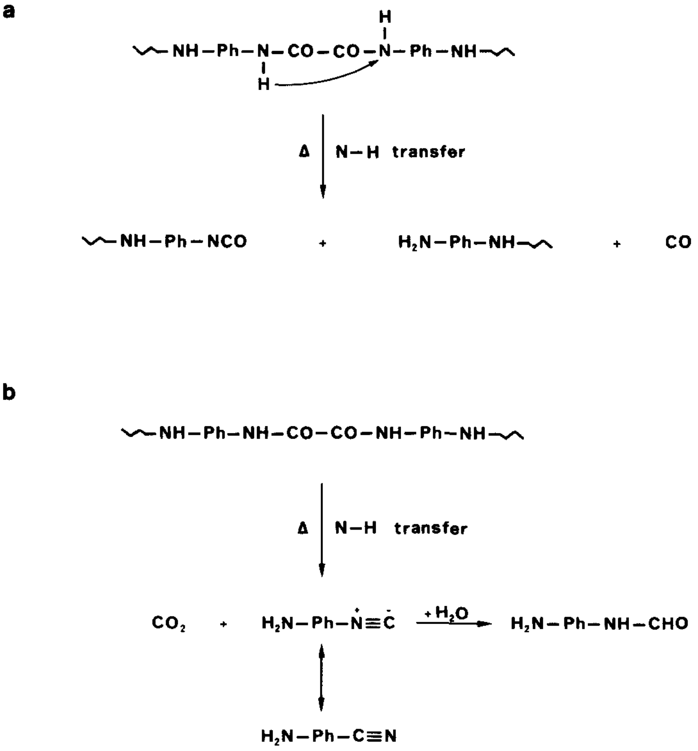
The results obtained in the DPMS analysis of the aromatic polyoxamide IV indicate that this polymer principally decomposes via a N–H hydrogen transfer process with formation of compounds having amine and/or isocyanate end groups (*Scheme IVa*). In fact in the CI mass spectrum in *Figure 4* peaks corresponding to protonated molecular ions of compounds with diamine end groups (*m*/*z* = 109 and 271) and with amine and isocyanate end groups (*m*/*z* = 135 and 297) are present (*Table 5*). Besides the reaction shown in *Scheme IVa*, another reaction takes place during the thermal degradation of this polymer. It consists of a N–H hydrogen transfer process, with loss of carbon dioxide. This process leads to the formation of compounds with amine and isonitrile end groups (*Scheme IVb*). These compounds undergo further reactions: (a) addition of water to the isonitriles with formation of formamides[27], present in the CI mass spectrum in *Figure 4* at *m*/*z* = 137 and 299 (*Table 5*); (b) thermal rearrangement of isonitriles to nitriles[28]. In fact, it is well known that the nitrile is thermodynamically strongly favoured at higher temperatures, and in the CI mass spectrum in *Figure 4* intense peaks corresponding to the protonated molecular ions of compounds with amine and nitrile end groups are observed at *m*/*z* = 119 and 281 (*Table 5*).

The results obtained in the DPMS analysis of the aliphatic polyoxamide V indicate that the thermal degradation of this polymer proceeds via a β C–H hydrogen transfer process, with formation of compounds with olefin and amide end groups (*Scheme V*). In fact, the base peak of the CI mass spectrum in *Figure 5* at *m*/*z* = 115 (*Table 6*) is the protonated molecular ion of the compound:

$$CH_2{=}CH{-}NH{-}CO{-}CO{-}NH_2$$

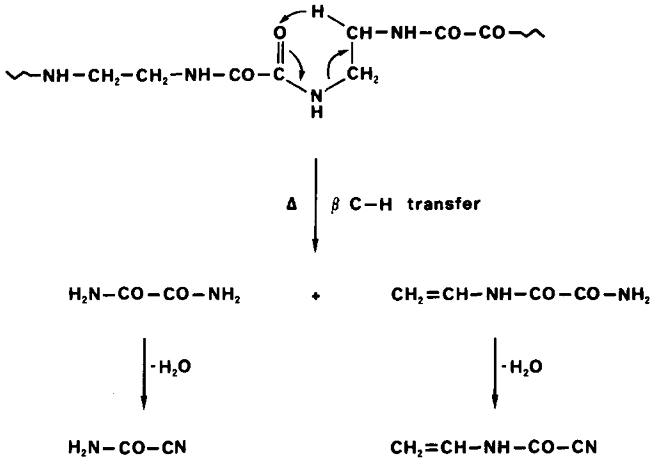
Primary pyrolysis products containing amide end groups undergo further thermal decompositions, with formation

Scheme IV



Scheme IV Thermal decomposition processes for polyoxamide IV

Scheme V



Scheme V Thermal decomposition processes for polyoxamide V

of compounds with nitrile end groups (*Scheme V* and *Table 6*). Inspection of the CI mass spectrum in *Figure 6* shows that these compounds are present at $m/z=97$ and 71 (*Table 6*). Also in this case, the presence of secondary thermal products indicates that the timescale of the DPMS experiment is too slow to prevent further thermal reactions.

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