Thermal Decomposition Processes in Aliphatic–Aromatic Polyamides Investigated by Mass Spectrometry

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ABSTRACT: The thermal decomposition processes of some aliphatic–aromatic polyamides derived from aliphatic dicarboxylic acids and aromatic diamines were studied by flash pyrolysis–gas chromatography–mass spectrometry and by direct pyrolysis–mass spectrometry, using both chemical ionization and electron impact modes. The results indicate that the thermal decomposition of these polyamides is strongly influenced by the structure of the aliphatic dicarboxylic acid units. In fact, the formation of compounds with succinimide and amine end groups is observed in the pyrolysis of the polyamides containing succinic units. In the pyrolysis of polyamides containing adipic units, on the other hand, the primary thermal degradation products are compounds with amine and keto amide end groups. In the pyrolysis of the latter polyamides, secondary thermal fragments are also formed: cyclopentanone, carbon dioxide, and compounds with azomethine and isocyanate groups.

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, determination of copolymer composition and sequence distribution, identification of oligomers formed in the polymerization reactions, and identification of volatile additives contained in polymer samples.[1-3]

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

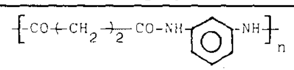
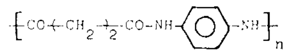
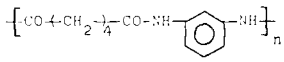
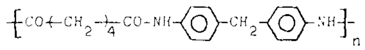
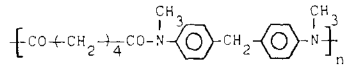
A general advantage of this technique is that pyrolysis is accomplished under high vacuum, and therefore the thermal decomposition products formed are volatilized and removed readily from the hot zone. This, together with the low probability of molecular collision and fast detection, reduces to a great extent the occurrence of secondary reactions, so that primary fragments are detected almost exclusively. Consequently, the information obtained is of particular importance in assessing 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 when other techniques are used.

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 spectrum of a polymer, the molecular ions of the thermal products 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, by making exact mass measurements, and by matching spectra of authentic samples with those obtained from the polymer.[1-6] In previous studies[1,3-6] we have investigated several classes of polymers by DPMS methods. Here we report a similar study for some aliphatic–aromatic polyamides (Table I).

Table I
Structure, Thermal Stability, and Viscosity of the Polyamides Investigated

	polymer	PDT[a]/°C	η_{inh}[b]
I		275	0.16[c]
II		295	0.11[d]
III		370	0.10[c]
IV		365	0.44[c]
V		430	0.29[c]

[a] Temperature of maximum decomposition rate of the polymer. [b] $\eta_{inh} = \ln \eta_r/c$; $c = 0.5$ g/dL. [c] In DMF + LiCl (3% by weight) at 30 ± 0.02 °C. [d] In H_2SO_4 at 40 ± 0.02 °C.

The thermal degradation of polyamides has been extensively studied by several techniques.[3,7-17] However, the thermal degradation of polyamides derived from aromatic diamines and aliphatic dicarboxylic acids (succinic or adipic acid) has not been investigated.

Our results indicate that the thermal decomposition of these polyamides is strongly influenced by the structure of the aliphatic dicarboxylic acid units. In fact, the formation of compounds with succinimide and amine end groups is observed in the pyrolysis of the polyamides containing succinic units. In the pyrolysis of polyamides containing adipic units, on the other hand, the primary thermal degradation products are compounds with amine and keto amide end groups. In the pyrolysis of the latter polyamides, secondary thermal fragments are also formed: cyclopentanone, carbon dioxide, and compounds with azomethine and isocyanate groups.

Experimental Section

Materials. Adipoyl and succinoyl chlorides were prepared and purified by standard techniques from dibasic acids and thionyl chloride. Other basic materials, i.e., *m*-phenylenediamine (model compound VI), *p*-phenylenediamine, 4,4′-diaminodiphenylmethane, and *N,N*′-dimethyl-4,4′-diaminodiphenylmethane, were commercial products appropriately purified before use.

Polymerization. Polymerizations were carried out by different methods. Here we report only those methods that yielded the

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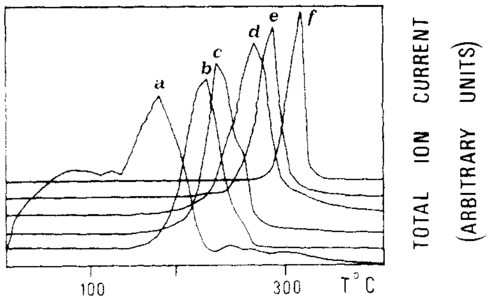


Figure 1. Single ion current (SIC) curves of (a) cyclopentanone (*m/z* 85), (b) 4,4′-diaminodiphenylmethane (*m/z* 199), and model compounds VIII (c) (*m/z* 265), IX (d) (*m/z* 331), X (e) (*m/z* 397), and XI (f) (*m/z* 463). Conditions: isobutane CI; heating rate 30 °C/min.

highest viscosities. Polyamides I and III were synthesized by interfacial methods, whereas polyamides II, IV, and V were synthesized by dispersion polycondensation.[18]

Polyamides I and III. In a typical interfacial polycondensation procedure (polymer I, Table I), the following chemicals were placed with stirring in a Waring blender precooled in a refrigerator: 1.56 g (0.01 mol) of succinoyl chloride dissolved in 30 mL of chloroform ($CHCl_3$) and 1.08 g (0.01 mol) of *m*-phenylenediamine and 2.12 g (0.02 mol) of sodium carbonate in 30 mL of water. The mixture was stirred for 5 min, and then an excess of water was poured in. $CHCl_3$ was removed in a rotary evaporator, and the polymer that precipitated was filtered, washed with methyl alcohol, and dried in vacuo at 40 °C for 24 h, with a yield of 60%.

Polyamides II, IV, and V. In a typical dispersion polycondensation procedure (polymer IV, Table I), the following chemicals were placed in a Waring blender precooled in a refrigerator: 2.75 g (0.015 mol) of adipoyl chloride dissolved in 36 mL of tetrahydrofuran (THF). To the rapidly stirred system were added in one application 2.97 g (0.015 mol) of 4,4′-diaminodiphenylmethane in 10 mL of THF and 3.18 g (0.030 mol) of sodium carbonate and 0.5 g of sodium lauryl sulfate in 50 mL of water. The mixture was stirred for 5 min, and then an excess of water was poured in. THF was removed by gentle warming under vacuum, and the polymer that precipitated was filtered, washed with water, and dried in vacuo at 50 °C. The crude polymer was dissolved in *m*-cresol, and the solution was filtered through a medium sintered-glass funnel and slowly precipitated in acetone. After standing overnight the polymer was filtered and dried in vacuo at 50 °C, with a yield of 100%.

Model Compound VII. *N,N′-m*-Phenylenebis(succinimide) (model compound VII) was synthesized in benzene solution from *m*-phenylenediamine and succinic anhydride. The compound was recrystallized from benzene/petroleum ether and was characterized by NMR and MS. Its melting point was 223–225 °C.

Reaction between Cyclopentanone and 4,4′-Diaminodiphenylmethane. A mixture of 6.0 g (0.030 mol) of 4,4′-diaminodiphenylmethane, 3.0 g (0.036 mol) of cyclopentanone (molar ratio 1:1.2), and 0.5 g of zinc chloride, used as a catalyst, was placed in benzene solution (150 mL) and refluxed for 2 h. After cooling, the solid residue was filtered off and the solvent was removed under vacuum.

The reaction mixture was introduced into the mass spectrometer by the direct insertion probe. The temperature of the probe was increased at a linear rate (30 °C/min), and the instrument was repetitively scanned in the chemical ionization mode from *m/z* 1000 to *m/z* 20, with a scan rate of 10 s/decade.

Only six strong peaks appeared in the CI mass spectra at increasing temperature. Their single ion current (SIC) profiles are shown in Figure 1. The first two curves belong to the reagents (cyclopentanone, protonated molecular ion *m/z* 85, and 4,4′-diaminodiphenylmethane, protonated molecular ion *m/z* 199). The remaining four peaks proved to be reaction products (compounds VIII–XI), which were identified by their molecular ions, as shown in Figure 2 (see below for further discussion).

Viscometry. Inherent viscosities ($\eta_{inh} = \ln \eta_r/c$; $c = 0.5$ g/dL) 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 I. Although inherent viscosities of some polyamides in Table I are not very high, their molecular weights are sufficiently high to avoid evaporation of undecomposed material. For a more extensive discussion of this point, see ref. 4b.

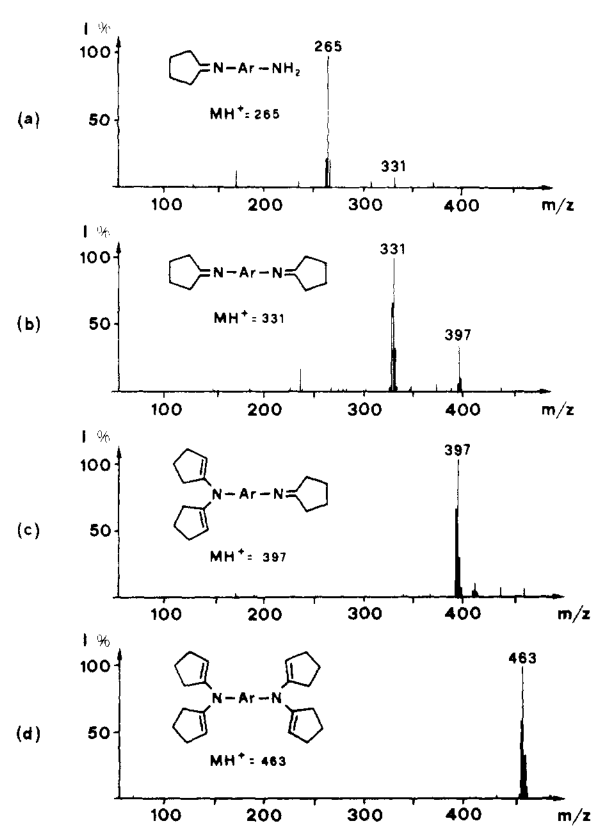


Figure 2. Isobutane CI mass spectra of model compounds VIII (a), IX (b), X (c), and XI (d).

Thermogravimetry. Thermal analyses were performed with a Perkin-Elmer TGS/2 apparatus in a nitrogen atmosphere (60 mL/min) at a heating rate of 10 °C/min. Polymer decomposition temperatures (PDT) of the investigated polyamides, as indicated by the maxima in their differential thermogravimetric curves, are listed in Table I.

Mass Spectrometry. A double-focusing Kratos MS 50S equipped with the standard electron impact or chemical ionization sources and a DS 55 data system were 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) and negative chemical ionization (NCI) mass spectra were obtained with isobutane or ammonia as reagent gases. Polymers were pyrolyzed directly in the ion source using standard Kratos probes, heated from 30 to 400 °C at a heating rate of 10 °C/min.

The mass spectra of polymer V were obtained on an LKB-9000 S mass spectrometer, equipped with an electron impact source; the heating rate was about 10 °C/min from 30 to 480 °C.

The reagent gases, isobutane (99.5%) and ammonia (99.998%), were purchased from Matheson Gas Products.

Flash Pyrolysis–Gas Chromatography–Mass Spectrometry (Py–GCMS). Flash pyrolysis experiments were carried out with a Pyroprobe Model 150 pyrolyzer from Chemical Data Systems. Pyrolyses were carried out at 700 °C per 5 s, in helium, using a coil probe. This temperature (dial setting temperature) was the most useful to obtain good chromatograms. The sample weights used ranged from 0.1 to 1 mg, and no changes in pyrolysis product distribution were observed.

Separation and identification of the pyrolysis products were performed by a Carlo Erba 4200 gas chromatograph combined with a Kratos MS 50S double-focusing mass spectrometer. GC separations were accomplished on a WCOT silica column (26 m

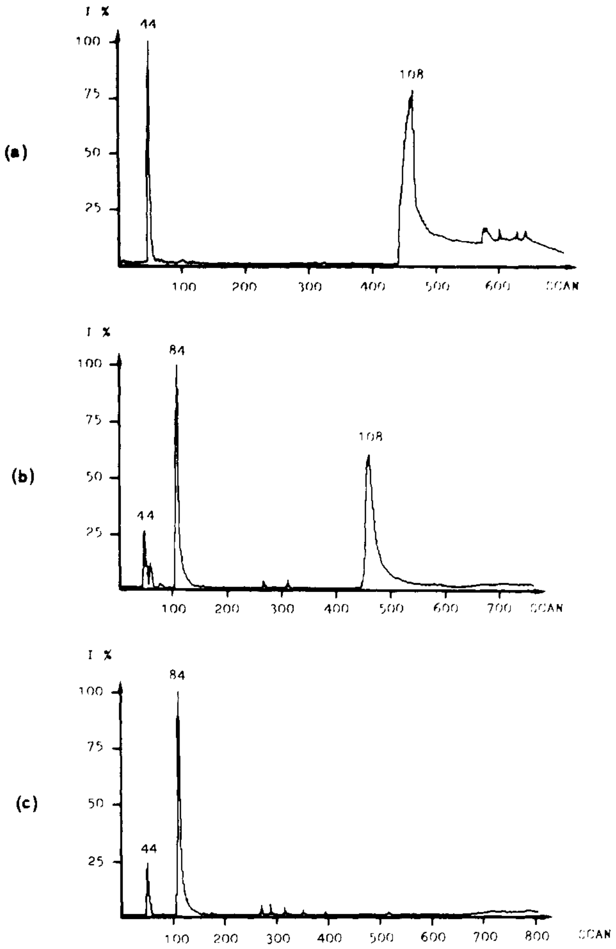


Figure 3. Total ion current chromatograms of the on-line flash pyrolysis–GCMS analysis of polyamide I (a), polyamide III (b), and polyamide IV (c). The compounds are identified by their value of *m*/*z*.

× 0.32-mm i.d.), coated with the stationary phase CP Sil 5 CB. The oven temperature program was as follows: 40 °C, initial time 5 min, heating rate 10 °C/min, final temperature 320 °C. Helium was used as the carrier gas.

Mass spectra were acquired by a Data General Eclipse/120 data system operating under Kratos DS 55 software. The mass spectrometer was scanned repetitively from *m*/*z* 500 to *m*/*z* 17 at a scan rate of 0.7 s/decade; the ionizing conditions were 18 eV.

Results

Thermal Stability. The thermal stabilities of the polyamides investigated, indicated by the maxima in their differential thermogravimetric curves (polymer decomposition temperatures, PDT), are reported in Table I. Temperatures of maximum volatilization rate, observed with the mass spectrometer by monitoring the total ion current (TIC) for the polymers in Table I, closely match those recorded by thermogravimetry.

This coincidence is not as surprising as it might appear on grounds that a mixture of compounds should distill at lower temperatures under vacuum than at atmospheric pressure. In fact, pyrolysis of polyamides in Table I occurs around 300–400 °C and the pyrolysis products distill simultaneously as soon as they are generated. Therefore the effect of vacuum on the evolution temperature is canceled.

The differences in the PDTs of these polymers suggest a difference in the mechanisms of thermal degradation.

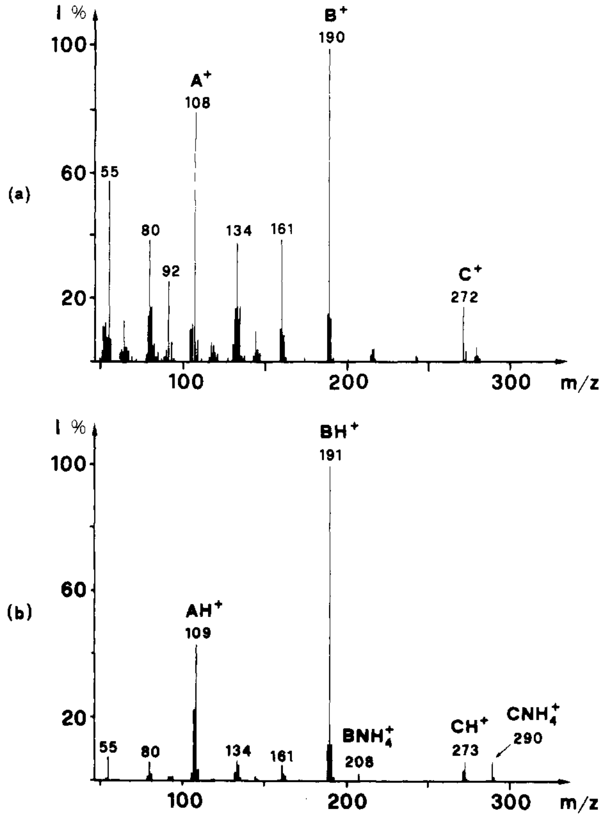


Figure 4. (a) EI mass spectrum (18 eV) and (b) ammonia CI mass spectrum of the products of thermal degradation of polyamide I at 275 °C.

Flash Pyrolysis–GCMS. In Figure 3a–c are reported the total ion current chromatograms of the on-line Py-GCMS of polyamides I, III, and IV, respectively. Chromatograms of polyamides II and V are not reported because they show the same behavior as polymers I and IV, respectively.

The chromatogram of polyamide I, shown in Figure 3a, exhibits two peaks with high intensity: carbon dioxide (MW = 44) at scan 48 and *m*-phenylenediamine (MW = 108) at scan 460 (Table II).

The chromatogram of polyamide III, shown in Figure 3b, exhibits three intense peaks: carbon dioxide (MW = 44, scan 48), cyclopentanone (MW = 84, scan 109), and *m*-phenylenediamine (MW = 108, scan 463) (Table III).

In contrast, the chromatogram of polyamide IV, shown in Figure 3c, exhibits only two peaks, corresponding to carbon dioxide (MW = 44, scan 51) and cyclopentanone (MW = 84, scan 112) (Table III). In this case, as expected from the high molecular weight of the 4,4′-diaminodiphenylmethane, the peak corresponding to the diamine is absent (Figure 3c).

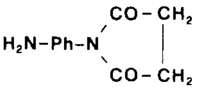
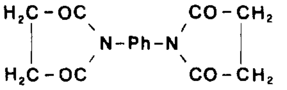
Direct Pyrolysis–Mass Spectrometry. Polyamide I. The electron impact (EI) mass spectrum of polymer I, recorded at a reduced electron energy of 18 eV and obtained in a DPMS experiment at a probe temperature of 275 °C, is shown in Figure 4a.

This mass spectrum shows several peaks due both to molecular ions of thermal decomposition products and to EI fragments. Molecular ions of pyrolyzates are present at *m*/*z* 108 (*m*-phenylenediamine), *m*/*z* 190 (*N*-(*m*-aminophenyl)succinimide), and *m*/*z* 272 (*N*,*N*′-*m*-phenylenebis(succinimide)) (Table II).

In order to confirm this interpretation, the ammonia CI mass spectrum of this polyamide, obtained at the same probe temperature, is reported in Figure 4b.

Peaks due to molecular species appear as protonated or NH_4^+ adduct ions in the ammonia CI mass spectrum. The peak at *m*/*z* 109 corresponds to the protonated molecular ion of *m*-phenylenediamine; peaks at *m*/*z* 191 and 208

Table II
Thermal Products Formed in the Thermal Degradation of Polyamides I and II

thermal product	symbol	m/z
$H_2N\text{-}Ph\text{-}NH_2$	AH^+	109
	BH^+ BNH_4^+	191 208
	CH^+ CNH_4^+	273 290

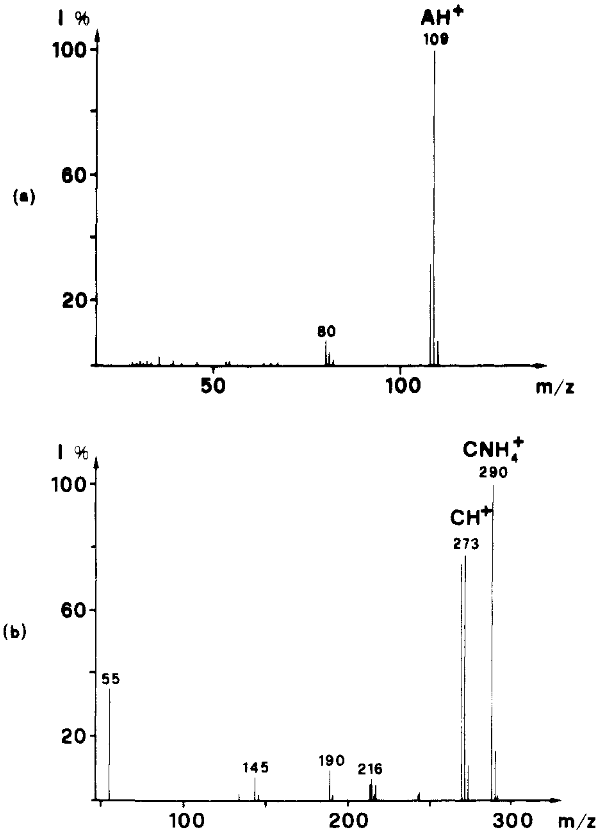


Figure 5. (a) Ammonia CI mass spectrum of model compound VI. (b) Ammonia CI mass spectrum of model compound VII.

correspond to the protonated molecular ion and to the NH_4^+ adduct of *N*-(*m*-aminophenyl)succinimide; peaks at *m/z* 273 and 290 correspond to the protonated molecular ion and to the NH_4^+ adduct of *N,N'*-*m*-phenylenebis(succinimide).

This interpretation is confirmed by comparison with the mass spectra of pure samples (model compounds VI (Figure 5a) and VII (Figure 5b)). In the ammonia CI mass spectrum of model compound VI (Figure 5a), the protonated molecular ion (*m/z* 109) is the only intense peak present. In Figure 5b is shown the ammonia CI mass spectrum of model compound VII. In this case, the mass spectrum shows the molecular ion (*m/z* 272) and the protonated molecular ion (*m/z* 273) with almost the same intensity, and its adduct with NH_4^+ (*m/z* 290). The comparison of the mass spectra in Figures 4b and 5b shows that the relative intensities of the peaks at *m/z* 272, 273, and 290 match well.

Structures assigned to compounds VI and VII in the mixture of pyrolysis products from polymer I were also confirmed by B/E-linked scanning.[19]

Polyamide II. The ammonia CI mass spectrum of polyamide II, obtained at a probe temperature of 295 °C in the DPMS experiment, is quite similar to that obtained for polyamide I (Figure 4b), and it is therefore omitted for brevity. This similarity indicates that the thermal decomposition process is similar in the two polymers and that the substitution of *m*-phenylenediamine with *p*-phenylenediamine does not affect the thermal degradation mechanism.

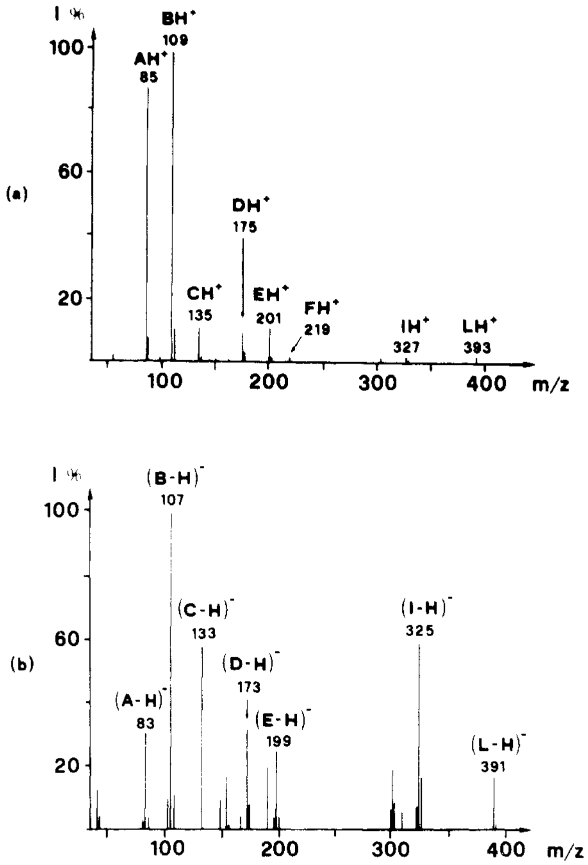


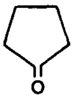
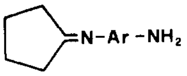
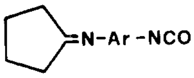
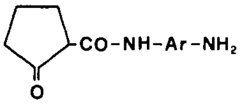
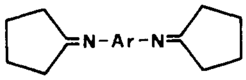
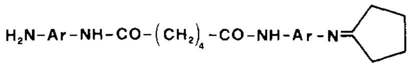
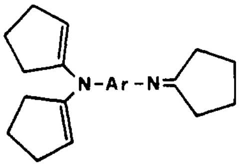
Figure 6. (a) Isobutane CI mass spectrum and (b) ammonia NCI mass spectrum of the products of thermal degradation of polyamide III at 370 °C.

Polyamide III. The isobutane CI mass spectrum of polyamide III, recorded at a probe temperature of 370 °C, is shown in Figure 6a. In this mass spectrum almost all peaks correspond to protonated molecular ions of primary or secondary thermal decomposition products (Table III). The base peak of the mass spectrum is the protonated molecular ion of *m*-phenylenediamine (*m/z* 109); the protonated molecular ion of cyclopentanone is also present at *m/z* 85 with high intensity. In this mass spectrum other peaks correspond to pyrolyzates having amino and isocyanate end groups (*m/z* 135), amino and keto amide end groups (*m/z* 219), and diamino end groups (*m/z* 327). Another family of compounds having azomethine groups is also present in the mass spectrum. These compounds show peaks at *m/z* 175, 201, and 393 (Table III).

The good quality of the positive CI mass spectrum in Figure 6a is confirmed by the negative CI mass spectrum, obtained at a probe temperature of 370 °C using ammonia as reagent gas, reported in Figure 6b. As can be observed from comparison of the two mass spectra, molecular ions appear as $(M-H)^-$ peaks in the negative CI mass spectrum (Figure 6 and Table III).

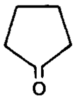
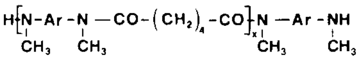
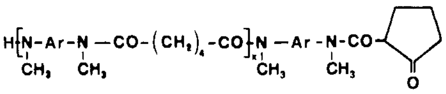
Polyamide IV. The isobutane CI mass spectrum of polymer IV, obtained at a probe temperature of 360 °C, is reported in Figure 7. Peaks corresponding to compounds formed by thermal decomposition appear in the mass spectrum as protonated molecular ions.

Table III
Thermal Products Formed in the Thermal Degradation of Polyamides III and IV

thermal product[a]	symbol	m/z	
		polymer III	polymer IV
	AH+	85	85
$H_2N-Ar-NH_2$	BH+	109	199
$OCN-Ar-NH_2$	CH+	135	225
	DH+	175	265
	EH+	201	291
	FH+	219	309
	GH+		331
$H_2N-Ar-NH-CO-(CH_2)_4-CO-NH-Ar-NH_2$	IH+	327	
	LH+	393	
	MH+		397

[a] Ar = *m*-phenylene for polymer III; Ar = 1,4-C_6H_4-CH_2-1,4-C_6H_4 for polymer IV.

Table IV
Thermal Products Formed in the Thermal Degradation of Polyamide V

thermal product[a]	symbol	m/z
	A+	84
 $H\left[\underset{CH_3}{N}-Ar-\underset{CH_3}{N}-CO-(CH_2)_4-CO\right]_x\underset{CH_3}{N}-Ar-\underset{CH_3}{NH}$	B+, $x = 0$ C+, $x = 1$ D+, $x = 2$	226 562 898
	E+, $x = 0$ F+, $x = 1$	336 672

[a] Ar = 1,4-C_6H_4-CH_2-1,4-C_6H_4.

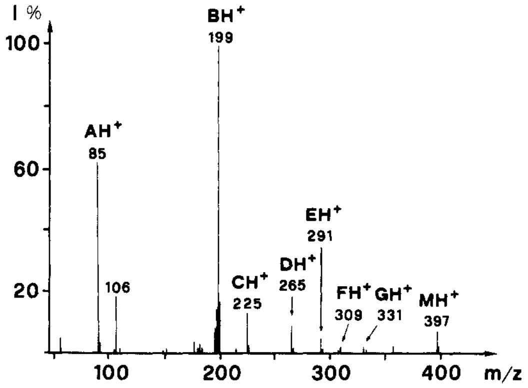


Figure 7. Isobutane CI mass spectrum of the products of thermal degradation of polyamide IV at 360 °C.

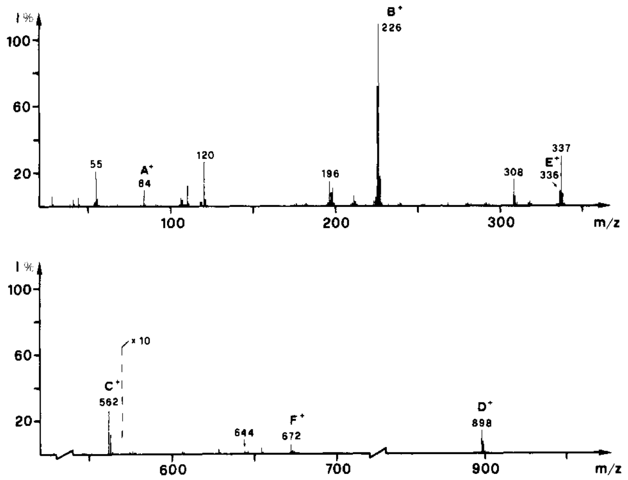


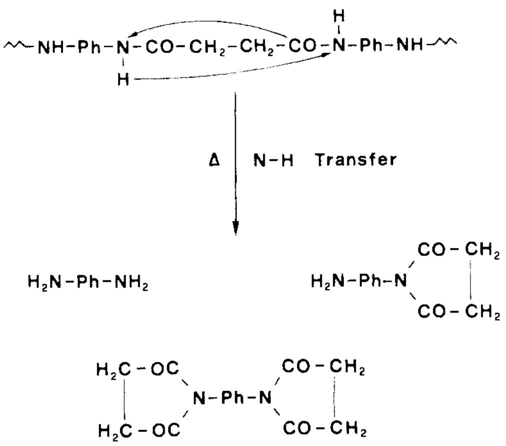
Figure 8. EI mass spectrum (18 eV) of the products of thermal degradation of polyamide V at 430 °C.

The pyrolysis products formed from polyamide IV are similar to those generated from polyamide III except, of course, for the different molecular weights of 4,4′-diaminodiphenylmethane and *m*-phenylenediamine (Table III). This indicates that the two polymers undergo a similar thermal decomposition process.

Polyamide V. The EI mass spectrum, recorded at a reduced electron energy of 18 eV and obtained at a probe temperature of 430 °C, is reported in Figure 8.

This mass spectrum exhibits abundant peaks corresponding to the molecular ions of compounds having diamine end groups (*m/z* 226 (base peak of the spectrum), 562, and 898), amine and keto amide end groups (*m/z* 336

Scheme I
Primary Thermal Decomposition Process for Polyamides I and II



and 672), and cyclopentanone (m/z 84) (Table IV).

Other peaks present in the mass spectrum are EI fragments from the thermally formed compounds. In fact, the peak at m/z 55 comes from cyclopentanone (m/z 84), and peaks at m/z 225, 211, 196, 120, and 106 come from *N*,*N'*-dimethyl-4,4'-diaminodiphenylmethane (m/z 226). Peaks at m/z 308 and 644 come from molecular ions at m/z 336 and 672, respectively, by the loss of 28 mass units. This loss is confirmed by the presence of metastable peaks.

Thermal Decomposition Processes. Problems in detecting significant pyrolysis products in condensation polymers are well-known,[3] and we have resorted to a combination of Py–GCMS and DPMS in order to collect more complete information on the polyamides investigated (Table I).

Py–GCMS differs from DPMS in that a very fast heating rate (up to 100 °C/ms) is used; often extensive fragmentation of the polymer chain occurs in Py–GCMS, and principally low molecular weight compounds are generated. Although high molecular weight compounds may also be formed, they cannot be eluted from the GC column or may undergo further thermal degradation because of the relatively long residence time at high temperature and the occurrence of secondary thermal degradation processes is observed.

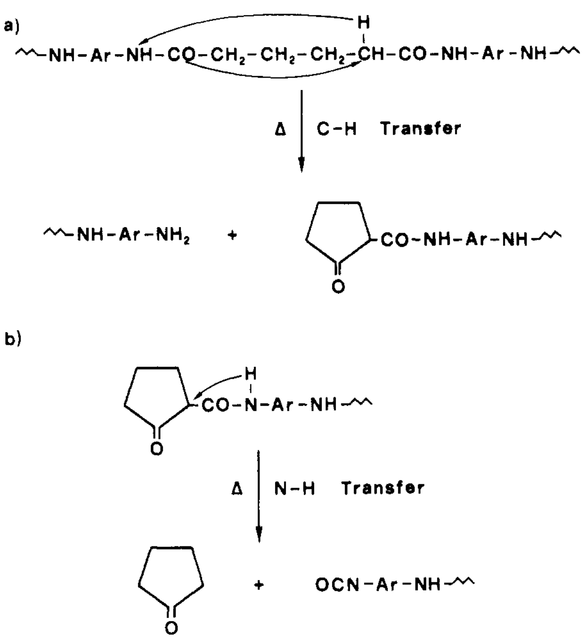
Chromatograms in Figure 3, corresponding to polyamides I, III, and IV, exhibit peaks identified as carbon dioxide, cyclopentanone, and phenylenediamine.

The presence of carbon dioxide is not observed in DPMS spectra of these polyamides (Figures 4–8), and therefore it may be concluded that the formation of CO_2 is due to a secondary thermal process.

The results obtained in the DPMS analysis of polymers I and II (Figure 4, Table II), indicate that these polymers decompose via an N–H hydrogen-transfer process with formation of amine and succinimide end groups (Scheme I). Therefore, the pyrolytic breakdown of polyamides I and II, as reported in Scheme I, leads to the formation of *m*- or *p*-phenylenediamine (MW = 108), *N*-(*m*-aminophenyl)- or *N*-(*p*-aminophenyl)succinimide (MW = 190), and *N*,*N'*-*m*- or *N*,*N'*-*p*-phenylenebis(succinimide) (MW = 272), respectively (Table II, Figure 4a). The above compounds are all primary thermal decomposition products.

Inspection of the data obtained for polymers III, IV, and V, with three different aromatic diamines and adipic acid (Table I), indicates that these polymers decompose via a C–H hydrogen transfer to the nitrogen atom with formation of compounds having amine and keto amide end groups (Scheme IIa). In fact, mass spectra in Figures 6–8 show several peaks that can be assigned to the above compounds (Tables III and IV). Peaks corresponding to diamines are present at m/z 109 and 327 in Figure 6a for polymer III (Table III), at m/z 199 in Figure 7 for polymer IV (Table III), and at m/z 226, 562, and 898 in Figure 8 for polymer V (Table IV). Compounds with amine and keto amide end groups are present at m/z 219 and 309 for polymers III and IV respectively (Table III), and at m/z 338 and 672 for polymer V (Table IV).

Scheme II
Thermal Degradation Processes for Polyamides III and IV (Reactions a and b) and for Polyamide V (Reaction a)



These primary thermal products further decompose with formation of secondary thermal fragments by an N–H hydrogen transfer to the α carbon atom of the keto amide compound with formation of cyclopentanone and of products with isocyanate end groups (Scheme IIb).

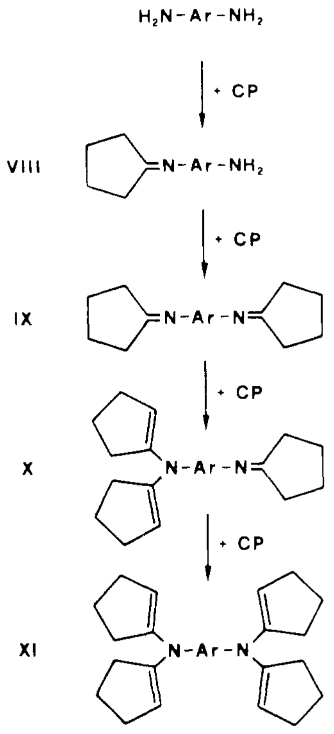
Further thermal reactions occur among the products formed in the thermal decomposition of polymers III and IV. In Scheme III are reported compounds VIII–XI, originating from the reaction of cyclopentanone with 4,4'-diaminodiphenylmethane (see Experimental Section and Figures 1 and 2). These compounds are also found in the DPMS spectra of polymer IV (Figure 7 and Table III), indicating that the time scale of the DPMS experiment is too slow in this case to prevent secondary reactions.

As pointed out above, if the pyrolytic process consists of primary, secondary, and further degradation processes, the mass spectra of decomposition products might change as the temperature is increased, because linear temperature programming is used. So single ion current (SIC) profiles of decomposition products might be helpful to understand the decomposition process, and different profiles should be observed. However, this difference, although detected in some cases,[1,4] is not always observed. A pertinent example is given by pyrolysis of poly(vinyl chloride) in the presence of Sb_2O_3, where HCl and $SbCl_3$ are simultaneously evolved although originating from successive thermal processes.[20]

In the present case, the SIC curves all have similar profiles and therefore are not particularly meaningful in this respect.

Carbon dioxide is not observed in the mass spectra in Figures 6 and 7. However, in the chromatograms in Figure

Scheme III
Further Thermal Reactions among Pyrolysis Products



CP = cyclopentanone

3, CO_2 is observed. It is likely that it originates from the pyrolysis of isocyanates (Scheme IIb), which are detected intact by DPMS (Table III), whereas they may undergo further degradation in the Py-GCMS experiments.

In the case of polymer V, the primary thermal decomposition mechanism is analogous to that of polymers III and IV. In fact, compounds similar to those observed for polymers III and IV are formed (Table IV). *N*-Methyl substitution should prevent the occurrence of the reaction shown in Scheme IIb, but small amounts of cyclopentanone are nevertheless present among the pyrolysis products (Figure 8 and Table IV). It therefore may be hypothesized that cyclopentanone is formed from carboxylic acid end groups, as already proposed by Wiloth.[17]

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Registry No. I (copolymer), 55425-95-1; I (SRU), 55445-71-1; II (copolymer), 55426-01-2; II (SRU), 55445-65-3; III (copolymer), 31451-66-8; III (SRU), 25949-52-4; IV (copolymer), 86924-58-5; IV (SRU), 52216-11-2; V (copolymer), 86893-64-3; V (SRU), 86893-41-6; VII, 76304-78-4; *m*-$H_2NC_6H_4NH_2$, 108-45-2; 4,4'-$H_2NC_6H_4CH_2C_6H_4NH_2$, 101-77-9; succinic anhydride, 108-30-5; cyclopentanone, 120-92-3.

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On the Structure of the Quenched Mesomorphic Phase of Isotactic Polypropylene

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ABSTRACT: The measured wide-angle X-ray diffraction intensity of the quenched mesomorphic phase of isotactic polypropylene is compared with the Fourier transforms of various models of chain aggregates. The calculations were performed on small bundles of threefold helices packed as in the hexagonal (β) and monoclinic (α) forms and on more disordered models showing both hexagonal and monoclinic features. Our results indicate that, in addition to the local parallelism of chains, a fairly high correlation of distances must be present within each chain and between neighboring chains in mesomorphic polypropylene. The local correlations between chains are probably nearer to those characterizing the crystal structure of the monoclinic form than to those characterizing the structure of the hexagonal form.

Introduction

The occurrence of a partially ordered phase (mesomorphic phase) together with an amorphous phase in rapidly quenched samples of isotactic polypropylene (i-PP) was pointed out many years ago.[1-3] On the basis of X-ray diffraction patterns and IR spectra it was recognized[1,2] that in the partially ordered phase of i-PP the individual chains maintain the threefold helical conformation and the chains

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