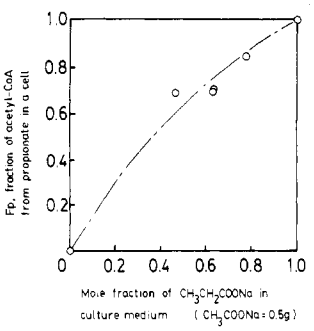

Figure 5. Relationship between F_p and mole fraction of propionate in the culture medium. F_p represents the fraction of acetyl-CoA from propionate to total acetyl-CoA in a cell.

the copolyester biosynthetic pathway shown in Figure 4. The fractions of acetyl-CoA arising from acetate and propionate as carbon sources were determined by using the values of ^{13}C enrichment at the specific sites of the copolyesters and the following relations:

$$21F_a + 1.1F_p = F(^{13}C) \quad (1)$$

$$F_a + F_p = 1.0 \quad (2)$$

Here, F_a and F_p represent the fractions of acetyl-CoA from ^{13}C-labeled acetate (21% ^{13}C) and natural abundance propionate (1.1% ^{13}C) to total acetyl-CoA in a cell, respectively, and $F(^{13}C)$ is the ^{13}C enrichment at the labeled sites of the copolyester. The results are given in Figure 5. The fracton F_p of acetyl-CoA from propionate is slightly higher than the mole fracton of propionate in the culture medium.

Acknowledgment. We thank Professor I. Karube for helpful discussions.

Registry No. (B)(V) (copolymer), 80181-31-3; PHB (SRU), 26744-04-7; PHB (homopolymer), 26063-00-3; $H_3CCH_2CO_2Na$, 137-40-6; H_3CCO_2Na, 127-09-3.

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Mechanism of Thermal Decomposition of Nylon 66

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ABSTRACT: The thermal decomposition mechanism of nylon 66 [poly(hexamethyleneadipamide)] has been investigated by direct pyrolysis into the mass spectrometer. Several methods have been used in order to identify compounds present in the pyrolysis mixtures: comparison of electron impact and chemical ionization spectra, accurate mass measurements, comparison with the mass spectra of authentic compounds, and tandem mass spectrometry (daughter and parent ions spectra). The results show that the thermal decomposition mechanism of nylon 66 occurs via a C–H hydrogen-transfer reaction to nitrogen with formation of compounds bearing amine and ketoamide end groups. These primary thermal products further decompose or react with formation of cyclopentanone, aminohexamethylene isocyanate, and compounds bearing amine and/or Schiff base groups. The synthesis of some key thermal decomposition compounds of nylon 66 has been performed, allowing comparison of authentic samples with pyrolysis products.

Introduction

The thermal decomposition of nylon 66 [poly(hexamethyleneadipamide)] has been the subject of several publications over the past years.[1,2] Formation of hexamethylenediamine (HMDA) and cyclopentanone (CP) in the pyrolysis was recognized already in earlier studies,[3–5] whereas the presence of the cyclic monomer I was later detected by Peebles et al.[6] among the volatile products originating from the pyrolysis of nylon 66.

$$\underbrace{NH\text{–}(CH_2)_6\text{–}NH\text{–}CO\text{–}(CH_2)_4\text{–}CO}_{I}$$

It is now understood[7] that nylon 66, and many other condensation polymers as well, contains cyclic oligomers formed during the polymerization reaction, so that compound I cannot be considered a pyrolysis product without further scrutiny.

Since the advent of modern pyrolysis mass spectrometry techniques,[8–10] the thermal degradation of nylon 66 has been intensively investigated, and several mass spectro-

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0024-9297/87/2220-2991$01.50/0

metric articles have appeared in the last decade.[11-18]

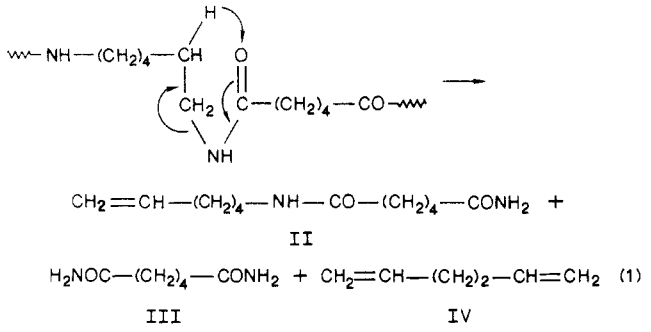
A general advantage of the direct pyrolysis mass spectrometry (DPMS)[8-10] is that pyrolysis is accomplished under high vacuum, and therefore the thermal products formed are volatilized and removed readily from the hot zone. This, together with fast detection and the low probability of molecular collision, 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 when 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 mass spectrum of a polymer, the molecular ions of the thermal products will appear mixed with the fragment ions formed in the ionizing step.

Dussel et al.[11] analyzed the pyrolysis of nylon 66 at 600 °C by field ionization mass spectrometry (FI-MS) and assigned structure II to a peak at m/z 226 (corresponding to the molecular weight of the repeating unit of this polymer).

This implies that the primary thermal decomposition process occurs by a β-C–H hydrogen-transfer reaction (eq 1) with formation of compounds II–IV.



It must be noted, however, that peaks with mass values corresponding to compounds III and IV are not present in the FI mass spectra.

Commercial granulates of nylon 66 where later investigated by pyrolysis electron impact mass spectrometry (EI-MS) by Luderwald et al.,[12] who assigned the peak at m/z 226 (nylon 66 repeat unit) appearing in the spectrum at 170 °C to the cyclic monomer I, contained in the polyamide and deriving from the polymerization reaction. The thermal decomposition products obtained at 400 °C were thought to be formed from a β-C–H hydrogen-transfer process leading to olefin and amide end groups (eq 1) and from an α-C–H transfer process, from the hydrogen in α-position to the carbonyl groups, leading to cleavage of the amide bond and formation of amine end groups.[12]

Some of the MS studies which appeared more recently on nylon 66 are essentially spectrometric in character.[15,16,18] Conway et al.[14] tentatively interpreted pyrolysis chemical ionization (CI) mass spectrometric data as indicating that the CI peak at m/z 227 (MH^+) has structure II and originates according to eq 1. Furthermore, following a suggestion of Wiloth,[19,20] who studied the thermal reactions of nylon 66 low molecular weight model compounds, Conway et al.[14] proposed that substituted cyclopentanone groups can be formed and can further degrade to yield Schiff bases.

Looking at the evidence provided by all these studies, however, one is forced to conclude that the structural assignments are only tentative and that no attempt has been made to identify the products present in the mass spectrum of the multicomponent mixture produced in the pyrolysis of nylon 66. All the authors[11-18] appear to assume that the primary thermal decomposition process is that described in eq 1, although this would leave unexplained the presence of cyclopentanone and of other products. Furthermore, several authors have reached diverging conclusions on the structure of peaks observed in their mass spectra.[11-18]

Several methods are available today in the standard mass spectrometric practice in order to identify compounds present in mixtures: (a) comparison with the mass spectra of authentic compounds; (b) tandem mass spectrometry to compare daughter and parent ions spectra; (c) accurate mass measurements; (d) soft ionization techniques, such as chemical ionization, to simplify complex ion fragmentation present in EI mass spectra.

We have used these techniques, in combination with the synthesis of some key compounds, in order to reinvestigate the thermal decomposition of nylon 66 by DPMS.

Our evidence disproves the assumption that nylon 66 decomposes by the β-C–H hydrogen-transfer reaction in eq 1, favoring instead a decomposition mechanism occurring via a C–H hydrogen transfer to nitrogen with formation of compounds having amine and ketoamide end groups. These primary thermal products further decompose or react with formation of cyclopentanone and compounds bearing amine and/or Schiff base groups.

Experimental Section

Materials. Adipoyl chloride was prepared and purified by a standard technique from adipic acid and thionyl chloride. Other basic materials, i.e., hexamethylenediamine, cyclopentanone, methyl 2-oxocyclopentanecarboxylate, and ethylene glycol, were commercial products appropriately purified before use.

Nylon 66 was synthesized by interfacial polycondensation, as described by Morgan.[21] The inherent viscosity ($\eta_{inh} = \ln \eta_r/c$; c = 0.5 g/dL), measured in a Desreux-Bishoff suspended level viscometer at 30 ± 0.01 °C, using m-cresol as solvent, was η_{inh} = 1.12. The polymer decomposition temperature (PDT), obtained by using a Perkin-Elmer TGS/2 apparatus in a nitrogen atmosphere (60 mL/min) at a heating rate of 10 °C/min, as indicated by the maximum in the differential thermogravimetric curve, was 410 °C.

Extraction of Oligomers from Nylon 66. Nylon 66 was extracted in a Soxhlet apparatus with methanol for 96 h. Methanol was evaporated and the residue was dried at 60 °C under vacuum, overnight.

The residue was analyzed by HPLC[22] and mass spectrometry. Peaks in the HPLC tracing were identified by MS as corresponding to monomer and dimer, after trapping the components at the exit of the column: HPLC column, Lichrosorb RP 8 5 μm (SUPELCO); eluent, CF_3CH_2OH 40%/H_2O 60% (density = 1.186); oven temperature, 50 °C; flow rate, 0.8 mL/min; detector, UV 205 nm.

Synthesis of Compounds V–VII (Scheme I). A mixture of 3.48 g (0.030 mol) of hexamethylenediamine, 3.03 g (0.036 mol) of cyclopentanone (molar ratio of 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 ($ZnCl_2$) 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 (20 °C/min) and the instrument was repetitively scanned in the chemical ionization mode, using isobutane as reagent gas, from m/z 1000 to m/z 20, with a scan rate of 10 s/decade.

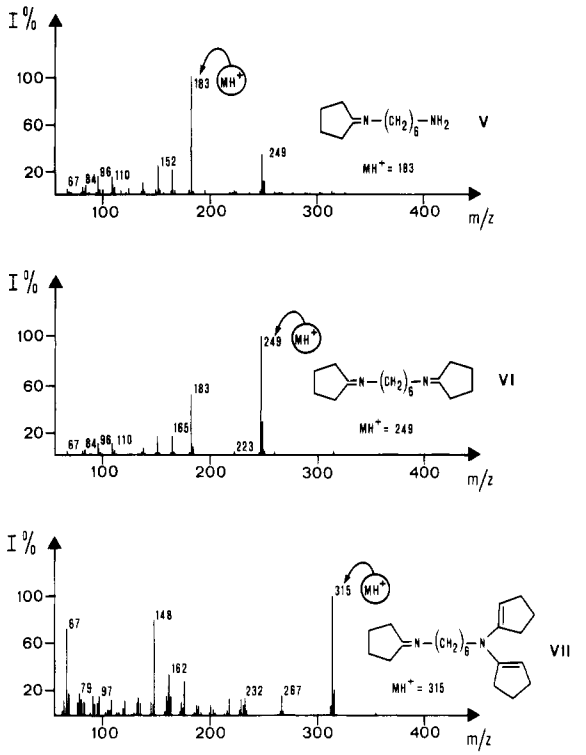
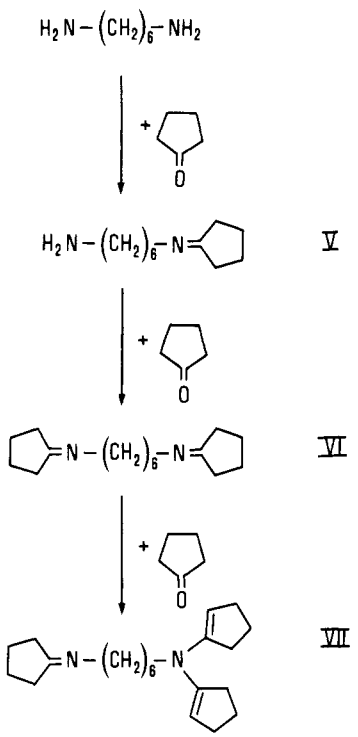


Figure 1. Isobutane CI mass spectra of authentic compounds V–VII.

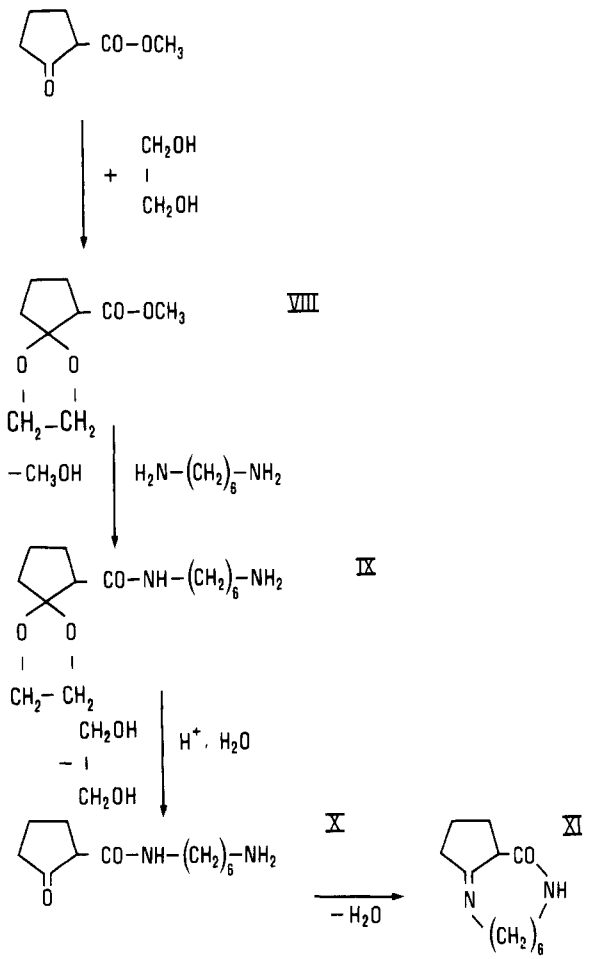
Scheme I
Reactions between Hexamethylenediamine and Cyclopentanone



Only five strong peaks appeared in the CI mass spectra at increasing temperature. The first two peaks belong to the reagents (cyclopentanone and hexamethylenediamine). The remaining three peaks proved to be reaction products (compounds V–VII, Scheme I) which were identified by their molecular ions (Figure 1) and linked scanning mass spectrometry (see below for further discussion).

Synthesis of Compound XI (Scheme II). A mixture of 4.0 g (0.028 mol) of methyl 2-oxocyclopentanecarboxylate, 6.97 g (0.112 mol) of ethylene glycol (molar ratio 1:4), and 3 drops of dilute HCl, used as a catalyst, was placed in benzene solution (30 mL)

Scheme II
Pathway of Formation of Model Compound XI



and refluxed for 4 h. The water was conveniently removed by using a water separator (Markusson apparatus). After cooling and solvent removal, the ketal VIII was separated from the reaction mixture by using a separatory funnel.

The ketal VIII was characterized by ^{1}H NMR spectroscopy and chemical ionization mass spectrometry: ^{1}H NMR ($CDCl_3$, TMS as internal reference) δ 1.86 (6 H), 2.83 (1 H), 3.70 (3 H), 3.91 (4 H); isobutane CI-MS, m/z (I%) 188 (10), 187 (100), 157 (10), 155 (20), 113 (12), 112 (10), 100 (35), 99 (70).

In a three-necked flask, equipped with a condenser protected by a drying tube, was placed 3.48 g (0.03 mol) of hexamethylenediamine (HMDA). Whereas a nitrogen stream was continuously bubbled in the mixture, 1.86 g (0.01 mol) of ketal VIII (molar ratio 3:1) was slowly dropped into the mixture by a loading funnel. The reaction mixture, during the loading, was heated slowly in an oil bath to about 200 °C and maintained at that temperature over a period of 4 h. After cooling, the excess of hexamethylenediamine and the formed methyl alcohol were removed at 70 °C under vacuum.

Compound IX obtained was characterized by ^{1}H NMR spectroscopy and chemical ionization mass spectrometry: ^{1}H NMR ($CDCl_3$, TMS as internal reference) δ 1.38 (8 H), 1.82 (6 H), 2.28 (2 H), 2.70 (2 H + 1 H), 3.22 (2 H), 3.93 (4 H), 6.0 (1 H); isobutane CI-MS, m/z (I%) 272 (16), 271 (100), 241 (24), 172 (11), 171 (92), 155 (39), 100 (51), 99 (29), 98 (27), 86 (18), 85 (18), 84 (17), 83 (10).

Ketal amine compound IX, 1.0 g (0.0037 mol), obtained in the previous step, was placed in a mixture 1:1 water/methyl alcohol and HCl (1:3) was slowly added up to acid reaction. After 5 min, NaOH was added in order to neutralize the solution. Simultaneously to the formation of the ketone group (X), the compound reacted intramolecularly to give the corresponding Schiff base (XI). The compound formed was extracted with chloroform by using a separatory funnel.

Compound XI was characterized by ^{1}H NMR spectroscopy and chemical ionization mass spectrometry: ^{1}H NMR ($CDCl_3$, TMS

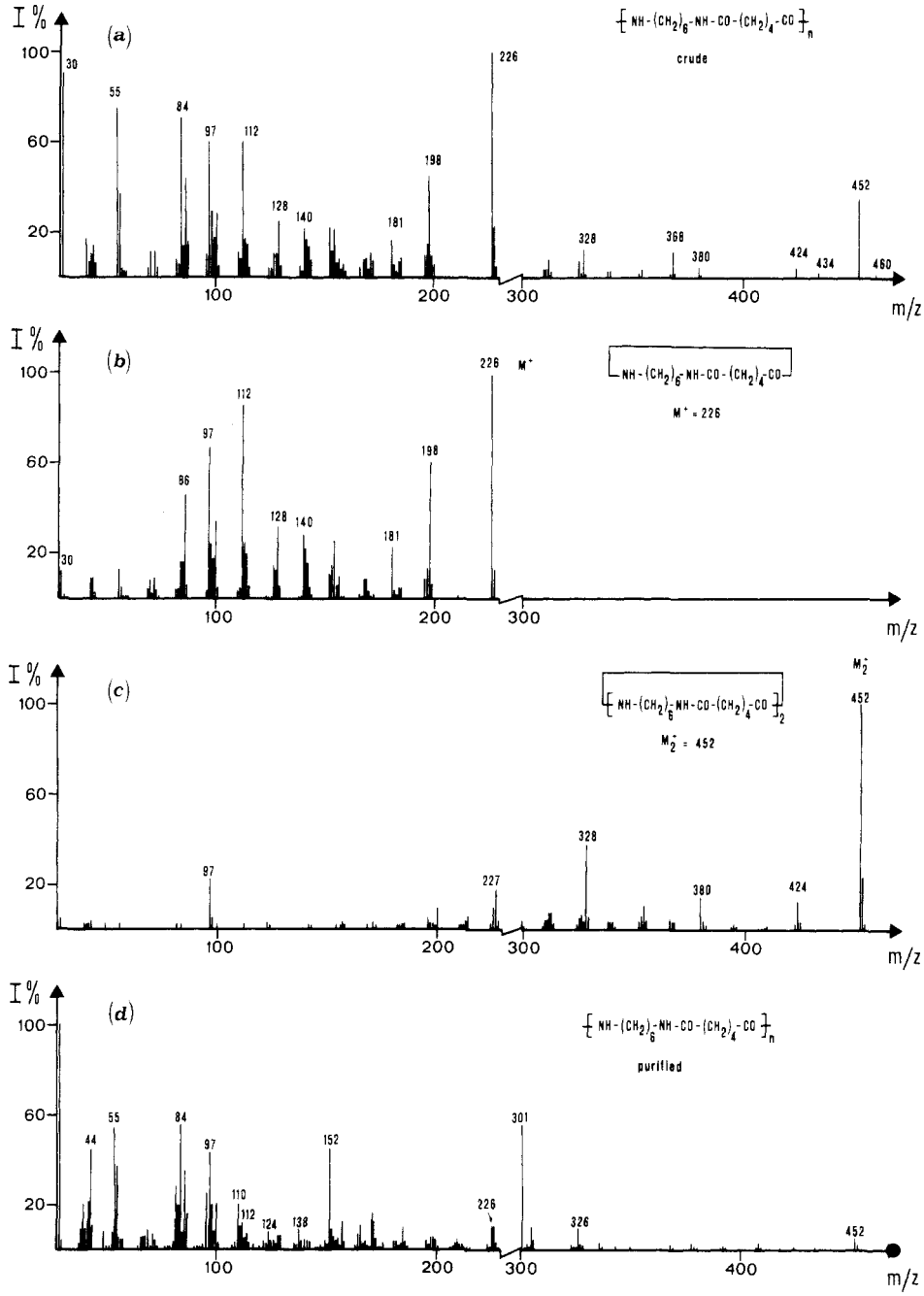


Figure 2. EI mass spectra (18 eV) of (a) products of thermal decomposition of crude nylon 66 at 400 °C, (b) cyclic monomer (m/z 226) at 150 °C, (c) cyclic dimer (m/z 452) at 250 °C, and (d) products of thermal decomposition of purified nylon 66 at 400 °C.

as internal reference) δ 1.40 (8 H), 1.90 (6 H), 2.40 (2 H + 1 H), 3.20 (2 H), 5.1 (1 H); isobutane CI-MS, m/z (I%) 210 (14), 209 (100), 208 (18), 166 (45), 165 (35), 153 (20), 152 (83), 138 (23), 124 (18), 111 (22), 110 (45), 98 (35), 97 (63), 96 (55), 84 (40), 83 (25), 82 (28), 69 (32), 67 (43).

Mass Spectrometry. A double-focusing Kratos MS 50S mass spectrometer (Nier-Johnson geometry) equipped with the standard electron impact or chemical ionization sources and a DS 55 data system was used to obtain mass spectra.

Electron impact (EI) and positive chemical ionization (CI) mass spectra were performed by scanning the magnet from m/z 1000 to m/z 20, with a scan rate of 10 s/decade. The ion source was maintained at 200 °C. CI mass spectra were obtained by using isobutane as reagent gas.

Perfluorokerosene was used as calibrant.

B/E (daughter ions) and B^2/E (parent ions)[23,24] scans were performed by using a linked scan unit at a scan rate of 20 s/decade and registered on an UV oscillograph.

Preliminary TG experiments in nitrogen indicated that nylon 66 pyrolysis is almost complete at 450 °C. Pyrolyses were therefore accomplished in the ion source of an LKB 9000S mass spectrometer by using a probe heatable up to 450 °C and also with the Kratos MS 50S mass spectrometer using standard Kratos probes, heated from 30 to 400 °C at a heating rate of 10 °C/min.

EI mass spectra of nylon 66 pyrolysates do not change significantly from the beginning to the end of the pyrolysis.

EI high-resolution mass spectra were performed with the Kratos MS 50S mass spectrometer at a resolution of 20.000. Accurate mass measurements in CI mass spectra were performed by using the exact masses measured in the EI spectra as reference, with the help of the DS 55 software (AMCOR).

Results and Discussion

The EI mass spectrum of crude nylon 66 obtained at a probe temperature of 400 °C is reported in Figure 2a and those of authentic samples of the cyclic monomer (m/z 226) and dimer (m/z 452) are reported in parts b and c of Figure 2, respectively.

Peaks at m/z 226 and 452, appearing in the mass spectrum of the crude nylon 66 sample (Figure 2a), are mainly due to preformed cyclic oligomers. They are in fact

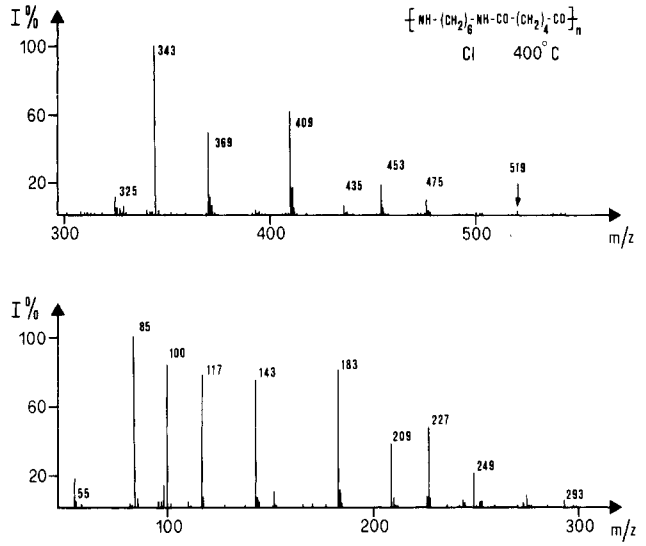
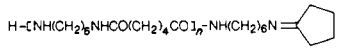
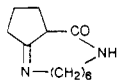
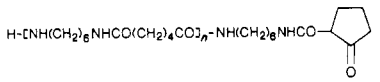
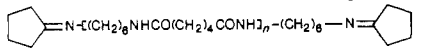
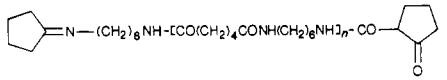
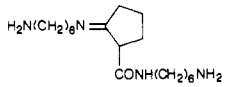


Figure 3. Isobutane CI mass spectrum of the products of thermal decomposition of purified nylon 66 at 400 °C.

Table I
Thermal Products Formed in the Thermal Decomposision of Nylon 66

thermal product		m/z (MH^+)
		85
$H-[NH(CH_2)_6NHCO(CH_2)_4CO]_n-NH(CH_2)_6NH_2$	$n = 0$ $n = 1$	117 343
$H-[NH(CH_2)_6NHCO(CH_2)_4CO]_n-NH(CH_2)_6NCO$	$n = 0$ $n = 1$	143 369
	$n = 0$ $n = 1$	183 409
		209
	$n = 0$ $n = 1$	227 453
	$n = 0$ $n = 1$	249 475
	$n = 0$ $n = 1$	293 519
		325

much weaker in the EI mass spectrum in Figure 2d, obtained at the same probe temperature and corresponding to the purified sample. These two preformed oligomers are still present in the spectrum at 400 °C (Figure 2a) because their distillation profile is overlapped to the polymer pyrolysis under our experimental conditions.

The EI mass spectrum of nylon 66 in Figure 2d, however, is complicated by the EI fragmentation of the molecular ion peaks of the thermal decomposition products.

In Figure 3 is reported the isobutane CI mass spectrum of purified nylon 66 recorded at 400 °C, which shows a remarkable simplification of the ion fragmentations and the appearence of new molecular ion species. The structural assignments of peaks appearing in Figure 3 are reported in Table I.

Accurate mass measurements, reported in Table II, allow one to distinguish unambiguously among several possible molecular formulas which correspond to the same nominal

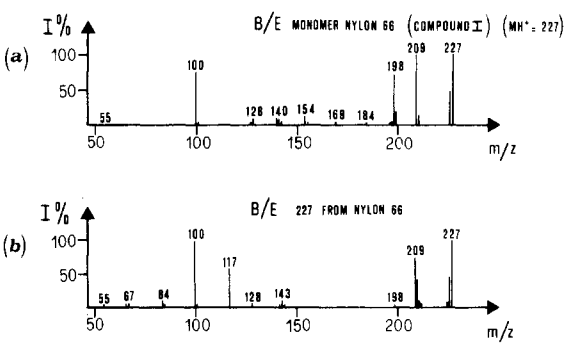


Figure 4. Isobutane CI daughter ion spectra of (a) an authentic cyclic monomer of nylon 66 and (b) the peak at m/z 227 from pyrolysis of purified nylon 66 (400 °C).

Table II
Accurate Mass Measurements of Peaks Appearing in the CI Mass Spectrum of Nylon 66

formula	exptl value	deviatn × 10^3
C_5H_9O	85.0667	+1.4
$C_6H_{17}N_2$	117.1384	−0.8
$C_7H_{15}N_2O$	143.1179	−0.5
$C_{11}H_{23}N_2$	183.1807	−5.4
$C_{12}H_{21}N_2O$	209.1647	−0.7
$C_{12}H_{23}N_2O_2$	227.1765	+0.6
$C_{17}H_{29}N_2O_2$	293.2221	−0.8
$C_{18}H_{39}N_4O_2$	343.3069	−0.4
$C_{19}H_{37}N_4O_3$	369.2857	−0.8
$C_{23}H_{45}N_4O_2$	409.3523	−1.9
$C_{24}H_{45}N_4O_4$	453.3437	−0.4

mass number. The lack of such measurements caused some erroneous assignments in earlier works.[11,12,14]

Linked scanning (B/E or B^2/E) measurements have been performed in order to confirm the identity of several peaks appearing in the CI mass spectrum in Figure 3. Isobutane CI daughter ion spectra of authentic samples of cyclopentanone (m/z 85), of HMDA (m/z 117), of HMDA monocyclopentanimine (m/z 183, compound V, Scheme I), and of HMDA dicyclopentanimine (m/z 249, compound VI, Scheme I) have been compared with the isobutane CI daughter ion spectra of the corresponding peaks in the mixture of pyrolysis products from nylon 66 in Figure 3. These four pairs of B/E spectra are omitted here for brevity. The pairs of spectra were essentially identical, thus confirming the structural assignments in Table I.

In parts a and b of Figure 4 are reported the isobutane CI daughter ion spectra corresponding to the authentic cyclic monomer of nylon 66 and to the peak at m/z 227 in the pyrolysis spectrum in Figure 3, respectively. They are different, establishing that the cyclic monomer is not a nylon 66 pyrolysis product.

Peaks in the CI mass spectrum in Figure 3 cannot be derived from the thermal decomposition mechanism described in eq 1; moreover, peaks corresponding to compounds of type III (m/z 145 + n226) and IV (m/z 83 + n226) are absent in the CI mass spectrum, ruling out the mechanism in eq 1 for the thermal fragmentation of nylon 66. In aromatic–aliphatic polyamides of formula

$$-[COPhCONH(CH_2)_xNH]_n- \qquad x = 2, 4, 6$$

where the thermal degradation mechanism involves a β-C–H hydrogen-transfer reaction, the three families of compounds II, III, and IV (eq 1) are present in the mass spectra and they represent the only pyrolytic compounds detected.[25]

The comparison of the B/E isobutane CI spectra of the protonated molecular ion of an authentic sample of compound XI (Figure 5a) and that of peak at m/z 209 in the

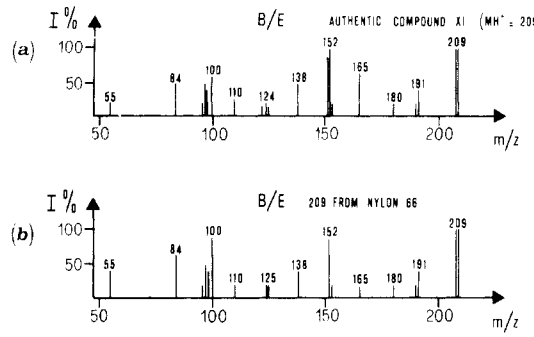
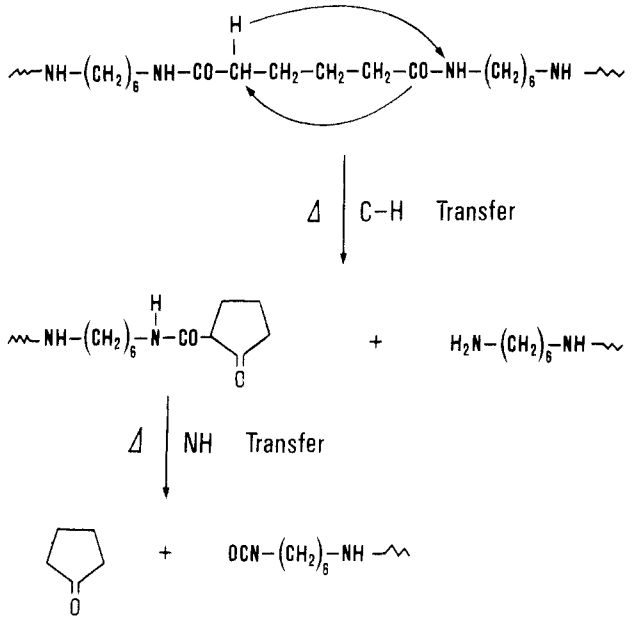


Figure 5. Isobutane CI daughter ion spectra of (a) authentic compound XI and (b) the peak at m/z 209 from pyrolysis of purified nylon 66 (400 °C).

Scheme III
Mechanism of Thermal Decomposition of Nylon 66



pyrolysis spectrum of nylon 66 (Figure 5b) confirms the structural assignment in Table I. Compound XI (see Scheme II and Experimental Section) is easily formed from compound X, because of the high tendency of its ketone and amine groups to react intramolecularly yielding the ketoimine XI.

Parent ion (B^2/E) spectra of the CI peak at m/z 100 in Figure 3 show that the latter is a fragment ion deriving from peaks at m/z 117, 143, 183, and 227, indicating that the fragment H_2N-$(CH_2)_6^+$ at m/z 100 is contained in the four parent peaks. Therefore this evidence characterizes the structure of the four compounds.

The overall spectral evidence presented here allows one to account for all the peaks appearing in the pyrolysis mass spectrum of nylon 66 (Figure 3) and to assign their structures as reported in Table I.

The structures of the pyrolysis products suggest that the primary thermal decomposition process occurring in nylon 66 is that involving a C–H hydrogen-transfer reaction to nitrogen with formation of compound X, HMDA, and of their higher homologues (Scheme III).

These primary thermal products further decompose by a hydrogen-transfer reaction (Scheme III) yielding cyclopentanone (MH^+ ion at m/z 85) and aminohexamethylene isocyanate (MH^+ ion at m/z 143) (Table I and Figure 3) and can thermally rearrange to compound XI (MH^+ ion at m/z 209) or react with cyclopentanone or HMDA to yield secondary thermal products, bearing Schiff base

Scheme IV
Further Thermal Reactions among Pyrolysis Products

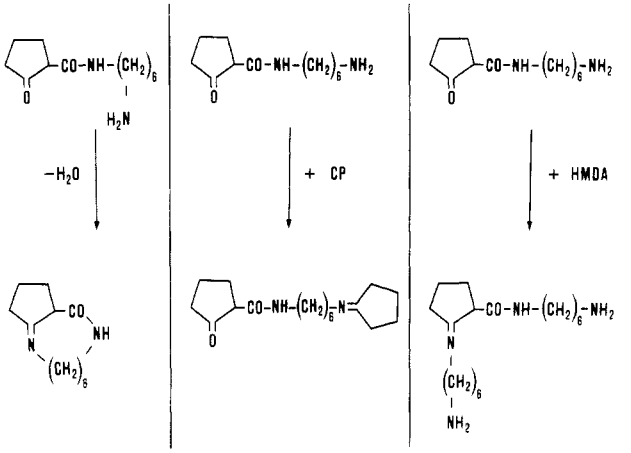
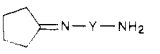
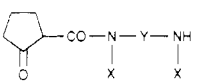
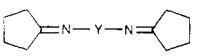


Table III
Thermal Products Formed in the Thermal Decomposition of Three Polyamides and of the Polyhydrazide

—[CO(CH₂)₄CONYN]ₙ—
X X

	m/z (MH^+)			
thermal product	X = H; Y = Ph	X = H; Y = $PhCH_2Ph$	X = CH_3; Y = $PhCH_2Ph$	X = H; Y = nihil
	85	85	85	85
HXN-Y-NXH	109	199	227	
H_2N-Y-NCO	135	225		
	175	265		99
	219	309	337	143
		331		

groups (MH^+ ions at m/z 293 and 325, respectively) (Scheme IV, Table I, and Figure 3). Ketoimines V and VI (MH^+ ions at m/z 183 and 249), present in the isobutane CI mass spectrum of pyrolysis products of nylon 66 (Figure 3), come from the reaction of cyclopentanone and HMDA, as indicated in Scheme I and shown in Figure 1 (Table I).

Further support to the mechanism in Scheme III comes from earlier findings[26,27] on the structure of the thermal decomposition products of some polyamides and of a polyhydrazide which contain the adipic acid unit (Table III). The isobutane CI mass spectra of these polymers show intense peaks due to molecular ions of pyrolysis products having cyclopentanone and amine end groups (Table III).

All these aliphatic polymers decompose via a C–H hydrogen transfer to the nitrogen atom, with formation of compounds having cyclopentanone unit end groups as in the case of nylon 66 (Scheme III). These primary thermal products further decompose with formation of secondary fragments by hydrogen-transfer processes.

It must therefore be concluded that the mechanism of thermal decomposition of nylon 66 proposed in Scheme III is common to polyamides containing adipic acid units, as we have observed in other instances.[26,27]

Acknowledgment. Partial financial support from the Italian Ministry of Public Education and from Consiglio Nazionale delle Ricerche (Roma) is gratefully acknowledged.

Registry No. I, 32131-17-2; V, 110295-55-1; VI, 110295-56-2; VII, 110295-57-3; VIII, 110295-58-4; IX, 110295-59-5; XI, 110295-60-8; $H_2N(CH_2)_6NH_2$, 124-09-4; $HO(CH_2)_2OH$, 107-21-1; cyclopentanone, 120-92-3; methyl 2-oxocyclopentanecarboxylate, 10472-24-9; (adipoyl chloride)(hexamethylenediamine) (copolymer), 28502-27-4.

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X-ray Diffraction from Liquid-Crystalline Copolyesters: Matrix Methods for Intensity Calculations Using a One-Dimensional Paracrystalline Model

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Received December 23, 1986

ABSTRACT: X-ray fiber diagrams of wholly aromatic liquid-crystalline copolyesters contain a series of aperiodic meridional maxima at positions that depend on the monomer ratio. Previous papers from this laboratory have shown that the positions and relative intensities of these maxima are predicted by a structure consisting of parallel extended chains of completely random monomer sequence. We present here a generalized approach for studying the diffraction characteristics of polyatomic monomers in stiff-chain systems with varied chemistries and microstructures. The random chain is most conveniently treated as a one-dimensional paracrystal with multimodal coordination statistics, and the use of matrices to define the neighbor probabilities leads to an efficient calculation of the scattering by nematic arrays of finite or infinite copolymer chains. Modification of the correlation statistics allows for investigation of the sensitivity of the X-ray data to nonrandom comonomer sequence distributions. The procedures also include consideration of nonlinearity of the chains, leading to determination of the correlation or persistence length for the stiff-chain conformation from the half-widths of the invariant peaks.

Introduction

Previous papers from this laboratory have described analysis of the structure of wholly aromatic melt-processable liquid-crystalline copolyesters. The X-ray fiber diagrams of copolyesters prepared, e.g., from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) show features unlike those reported previously for any other group of polymers, in that the intensity distribution is aperiodic along the chain axis direction. It has been shown that these data are predicted for an array of copolymer chains of completely random sequence. The aperiodic diffraction maxima arise due to structural correlations which are inherent in extended random copolymer chains. These copolyesters have also generated commercial interest in that high strength/high modulus fibers and high performance moldings can be obtained from the ordered melts. The synthesis and properties of these polyesters are the subject of numerous papers and patents (for reviews see ref 1–3). It has been found that the bulk properties of these copolymers are very sensitive to variations in the monomer chemistry.[4] There is also evidence for changes in the three-dimensional order as a result of thermal treatment, leading to an overall improvement in the properties of these systems.[5]

Figure 1 shows the intensity distribution along the meridian, as obtained by a $\theta/2\theta$ diffractometer, for five comonomer ratios. The observed meridional maxima are aperiodic, i.e., they are not orders of a simple repeat, and also shift in position with monomer ratio. The *d*-spacings of the meridional maxima are listed in Table I.

Modeling the structure of the copolyesters as an array of parallel chains with completely random monomer sequence leads to predicted X-ray scattering patterns that are in good agreement with the observed data.[6,7] The

0024-9297/87/2220-2997$01.50/0