

Thermal Degradation of Aliphatic Polyamides Studied by Field Ionization and Field Desorption Mass Spectrometry

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Synopsis

The aliphatic polyamides nylon 6.6, 6.9, 6.10, 6.12, 12.6, 12.10, and 12.12 of the diamine dicarboxylic acid-type were pyrolyzed in the ion source of a double-focusing mass spectrometer and the thermal degradation products were recorded by field ionization (FI) and field desorption (FD) mass spectrometry (MS). In the FI mode, several series of thermal degradation products differing in the number of polymer repeating units were detected up to 1000 Daltons. The main products were oligomers and, in addition, protonated dinitriles and various protonated nitriles are formed in large amounts except for nylon 6.6 and nylon 12.6. These two polymers form, in contrast to all other samples, large amounts of protonated amines and diamines. The technique employed allows distinction between oligomers already present in the original polymer and oligomers formed by thermal fission of bonds in the polymer chain. Reaction mechanisms are given that explain the products observed. High resolution experiments and accurate mass measurements were performed to confirm the proposed structures. In the FD mode, cationized oligomers (attached mostly to a sodium cation) were observed below 200°C with the dimers being the base peak for most samples. In contrast to the FI results, the monomers were only detected at very low intensities. Similarly, only weak signals for additional thermal degradation products were registered except for nylon 12.6. At higher temperatures the FD mass spectra gave protonated and doubly protonated oligomers in the high mass range up to 2000 Daltons, which resulted in complementary structural information about the polymers.

INTRODUCTION

Direct thermal degradation in combination with in-source MS is of increasing importance in the investigation of polymeric structures. Recently, several pyrolysis and ionization techniques for synthetic and biological polymers have been reviewed.¹ Predominantly molecular ions are observed in FI and FD spectra. As almost no mass spectrometric fragmentation takes place, the detection of thermal degradation products may be performed without previous separation of the complex mixtures.

In earlier work, the aliphatic polyamides nylon 6.6, 6.10, 4.10, 11.6, and 12.12 have been pyrolyzed at 170 and 400°C.² The pyrolyzates were recorded by electron impact (EI) MS. Cyclic and linear monomers and dimers were formed, but degradation products also arose from cleavage of the amide bond and cis-elimination.

The formation of oligomers attached to an alkali cation is the preferred ionization mechanism observed in FDMS.³ Following the thermal degradation reaction, $[M + Na]^+$ ions were reported for nylon 6.6⁴ and poly-(4,4'-dipiperidylamides).⁵ The thermal degradation products which formed the series

$[(M_n - 44) + \text{Na}]^+$, $[(M_n - 18) + \text{Na}]^+$, and $[(M_n - 84) + \text{Na}]^+$, suggest that cleavage of an amide bond, elimination of water and cleavage of the CH_2-CO bond take place. A series of $[(M_n - 110) + \text{Na}]^+$ ions was also observed. The corresponding pyrolysis products of nylon 6.6, which resulted from cleavage of an amide bond, have also been detected by FIMS⁶ with low intensities up to 300 Daltons. Pyrolysis products with amide, nitrile, alkyl and ω -alkenyl end-groups have been detected by FIMS of nylon 6.6. Further, fast pyrolysis at 550°C lead to splitting of the aliphatic chains⁷ to give hydrocarbons and hydrocarbons containing an amide group. Large quantities of dinitriles were formed from nylon 6.9, 6.10, 6.12, 12.10, and 12.12, cyclopentanone from nylon 6.6 and 12.6.

In earlier investigations, amines, diamines, cyclopentanone, and its derivatives were found by conventional pyrolysis studies.^{8,9} Mechanisms suggested for the primary degradation step have been discussed.¹⁰

In the present work, seven standard polyamides are investigated by soft ionization MS, the observed ions are tentatively assigned and thermal degradation mechanisms proposed. In particular, it was of interest to see whether ionization techniques such as FI and FD allow to detect high-mass signals of thermal degradation products, to investigate the general degradation pathways, and to yield structural information of the polymers.

EXPERIMENTAL

The experiments were performed on a Finnigan MAT 731 double-focusing mass spectrometer. In FI mode, the samples were heated in a temperature range from 50 to 750°C with a heating rate of about 1.5°C s⁻¹. In the FD mode, the samples were dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol and applied to the FD emitter. The pressure was about 10⁻³ Pa and the initial temperature was 50°C. The samples were heated by raising the emitter heating current from 10 to 35 mA (from 50 to 500°C). The vaporized molecules were ionized at an emitter potential of 8 kV, and a counter electrode potential of -3 kV. The mass ranges recorded for FI and FD spectra were 50–1000 and 100–2000 Daltons, respectively. The spectra were recorded electrically and averaged over 30–40 scans using the Finnigan MAT SS200 data system.

High resolution EI and FI mass spectra of nylon 6.10 were recorded using Ilford Q2 photoplates. The resolution was 10,000 for EI and 4000 for FIMS. The photoplate was evaluated by a Gaertner comparator and the Finnigan data system. In some cases, the accurate masses of the FI ions were determined by electrical detection, dynamic high resolution, and peakmatching.

The aliphatic nylon samples investigated in this work were generous gifts from Professor S. Tsuge, Department of Synthetic Chemistry, Nagoya University, Japan.

RESULTS AND DISCUSSION

Field Ionization Mass Spectrometry

Generally, predominant molecular ions of the thermal degradation products are observed in the whole mass range from 50 to 1000 Daltons and, in contrast to the results of Py-GC/MS,⁷ high-mass degradation products are detected.

Each type of degradation product forms ion series differing in the number of polymer repeating units. The mass signals observed corresponding to the main degradation products, its relative abundances and structures assigned are listed in Table I. The amounts of residual monomer present in the polymers are not included in the values of the relative abundances.

The degradation pathways depend greatly on the dicarboxylic acid unit. Three different main reactions occur, the formation of cyclic oligomers, of amines and nitriles. The spectra of nylon 6.6 and nylon 12.6 differ significantly from those of the other samples.

Figure 1 shows the thermogram of nylon 6.10, which represents the typical behavior of these condensation type nylon samples. The total count of all ions reaching the detector of the mass spectrometer and the count of the monomer at m/z 282 are given for the heating period from 50 to 750°C. The first maximum for the cyclic monomer seen at 280°C results from the evaporation of the residual monomer contained in the polymer, whereas the second maximum formed mainly above 450°C is a degradation product of the polymer chain. With FIMS, the monomer at m/z 282 is the major product detected in the temperature range from 200 to 400°C.

The integrated FI spectrum for nylon 6.10 recorded in the temperature range from 450 to 600°C is shown in Figure 2. This spectrum is shown as an example for all nylons except the adipic acid derivatives, nylon 6.6 and nylon 12.6. Oligomers, including the monomer, and protonated oligomers are observed at m/z 282, 283, 564, 565, 846, and 847. Previously, the observation of cyclic as well as open-chain oligomers has been reported.² Under FI conditions the formation of nitriles is a preferred degradation pathway as observed previously in Py-GC/MS studies.⁷ All nitriles observed are protonated in the FI mode. One of the most dominant ion series for nylon 6.10 is formed by protonated dinitriles at m/z 165, 447, and 729 containing 0, 1, and 2 polymer repeating units, respectively.

Several kinds of mononitriles are formed, in which the other end group is olefinic. Protonated nitriles containing all carbon atoms from the methylene groups of the carboxylic acid unit appear with moderate abundances at m/z 138, 420, and 702 as shown in Figure 2 and Table I. In agreement with the Py-GC/MS results,⁷ the formation of nitriles containing one methylene group less is strongly preferred. Mass signals assigned to these nitriles are seen in the FI spectrum at m/z 124, 406 and 688 forming the ion series F in Table I.

The formation of nitriles via a six-membered transition state,^{2,4,7} as illustrated in Scheme 1, explains the formation of the product series D, G and I in Table I. The corresponding saturated products of type I, 2 or 4 units higher in mass, are also seen. Generally, the products ending with olefinic groups (I) at both sides appear as $[I]^{++}$ and $[I + H]^+$ ions. In addition to the reaction described above, homolytic cleavages of the CH_2-NH bonds must be taken into account in the formation of these products.

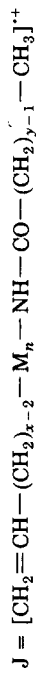
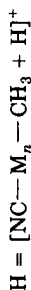
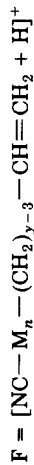
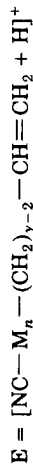
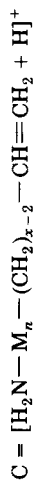
The base peak at the nominal mass 83 consists of different types of ions. High resolution EI and FI experiments and accurate mass measurements were performed to determine their elemental compositions. The main contribution determined by peak matching results from a doubly charged ion $[C_{10}H_{17}NO]^{2+}$ (83.5655 calculated, 83.5631 found) and, less intense, from an ion $[C_6H_{11}]^+$

TABLE I
Field Ionization Mass Spectrometry of Aliphatic Polyamides of the Type $(\text{NH}-(\text{CH}_2)_x-\text{NH}-\text{CO}-(\text{CH}_2)_y-\text{CO}-)_n$; m/z (relative abundance)

Type ^a	n^b	Nylon 6.6	Nylon 6.9	Nylon 6.10 ^c	Nylon 6.12	Nylon 12.6	Nylon 12.10	Nylon 12.12
A	1	226(18)	268(60)	282(60)	310(100)	310(48)	366(17)	394(58)
	2	452(88)	536(100)	564(64)	620(17)	620(3)	732(56)	788(32)
	3	678(26)	805(18)	846(3)	930(13)	930—		
B	0	117(1)	117(1)	117(1)	117—	201(7)	201—	201—
	1	343(16)	385(7)	399(2)	427(3)	511(100)	567—	595—
	2	569(100)	653(3)	681(2)	737—	821—	933—	989—
	3	795(1)	921—					
C	0	100(0.5)	100(6)	100(10)	100(3)	184—	184(6)	184—
	1	326(1)	368(15)	382(16)	410(16)	494(12)	550(19)	578(12)
	2	552(56)	636(15)	664(4)	720(1)	804—	916(11)	972—
	3	778(3)						
D	0	109(0.5)	151(11)	165(26)	193(2)	109—	165(7)	193(10)
	1	335—	419(48)	447(84)	503(8)	419—	531(13)	587(44)
	2	561—	687(84)	729(61)	813(12)	729—	897(45)	981(23)
E	0	82—	124(3)	138(3)	166—	82—	138(2)	166—
	1	308—	392(2)	420(4)	476(1)	392—	504(1)	560(12)
	2	534(2)	660(20)	702(10)	786(4)	701—	870(23)	954(19)
	3	760(1)						
F	0	68—	110(12)	124(14)	152—	68(1)	124(10)	152(8)
	1	294—	378(6)	406(14)	462(5)	378—	490(4)	546(7)
	2	520(3)	646(31)	688(24)	772(5)	688—	856(46)	940(19)
	3	746(1)						
G	0	209(0.5)	251(26)	265(41)	293(12)	293(3)	349(25)	377(40)
	1	435(2)	519(54)	547(72)	603(8)	693—	715(100)	771(100)
	2	661(9)	787(57)	829(21)	913(13)	913—		
	3	887—						

H	1	268—	310(7)	324(12)	352(5)	352—	408(5)	436(4)
	2	494(0.5)	578(41)	606(34)	662(5)	662—	774(30)	830(11)
	3	720(1)	846(2)	888(1)				
I	0	82—	82(7)	82(18)	82(2)	166—	166(12)	166—
	1	308—	350(1)	364(10)	392(5)	476—	532(7)	560(12)
	2	534(2)	618(18)	646(12)	702(3)	786—	898	954(19)
	3	760(1)	886(5)					
J	0	183—	225(3)	239(3)	267(1)	267(4)	323(1)	351(4)
	1	409(7)	493(11)	521(4)	577(2)	577(18)	689(5)	745(18)
	2	635(55)	761(16)	803(3)	887(1)	887		
	3	861(1)						

^aType—Structures tentatively assigned to FI signals (M = monomeric unit):



^b n = number of monomeric units.

^cThe base peak is at m/z 83.

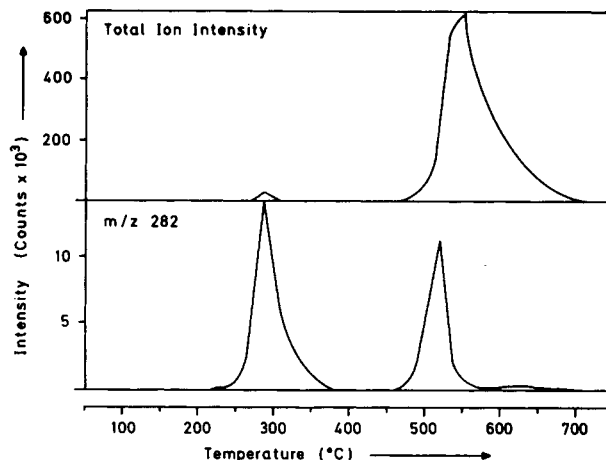


Fig. 1. FIMS of nylon 6.10: temperature dependence of the integrated ion counts and the formation of monomers.

(83.0861 calculated, 83.0863 found). High resolution data of other thermal degradation products are described below.

A six-membered ring similar to that shown in Scheme 1 may be involved in the formation of the nitriles type F and H. The rearrangement might take place at the opposite side of the amide bond, as shown in Scheme 2. The preference of type F nitriles to type E nitriles supports this assumption.

The spectra of nylon 6.6 and 12.6 differ strongly from those of the other five samples. Whereas oligomers are observed, dinitriles are absent. Mononitriles are formed in very low abundance. In contrast to the other five samples, these two polymers yield high abundances of amines and diamines although in the Py-GC/MS studies⁷ no amines were reported, and the amounts of dinitriles

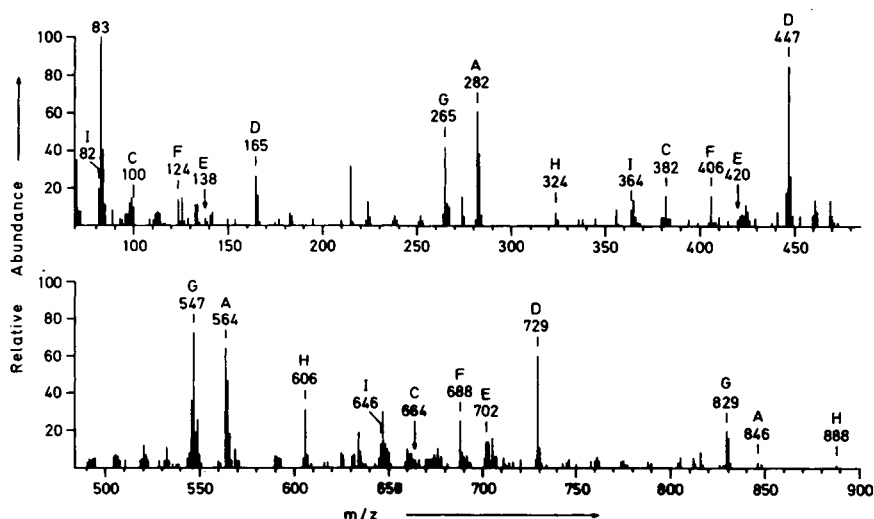


Fig. 2. FIMS of nylon 6.10: sum of five scans in the temperature range from 450 to 600°C. The letters refer to the corresponding products listed in Table I.

TABLE II
 High Resolution Mass Spectrometry of Nylon 6.10^a

Found		Calculated	Formula	Tentative structures
EI	FI			
282.2304	282.2256	282.2307	C ₁₆ H ₃₀ N ₂ O ₂	product A (polymer repeat unit)
—	100.1135	100.1126	C ₆ H ₁₄ N	product C
99.1057	—	99.1048	C ₆ H ₁₃ N	product C without protonation
—	165.142 ^b	165.1392	C ₁₀ H ₁₇ N ₂	product D
164.1378	—	164.1313	C ₁₀ H ₁₆ N ₂	product D without protonation
137.1237	^c	137.1204	C ₇ H ₁₁ N	product E without protonation
—	124.1047	124.1126	C ₈ H ₁₄ N	product F
123.1080	—	123.1047	C ₈ H ₁₃ N	product F without protonation
—	265.2227	265.2280	C ₁₆ H ₂₉ N ₂ O	product G
264.2209	—	264.2202	C ₁₆ H ₂₈ N ₂ O	product G without protonation
82.0817 ^d	82.075 ^b	82.0823	C ₆ H ₁₀	product I
83.0872	83.0782	83.0861	C ₆ H ₁₁	product I + H
165.1144	165.121 ^b	165.1153	C ₁₀ H ₁₅ NO	O=C—(CH ₂) ₈ —CN—H ²⁺ <i>m/z</i> 83.5656 plus one repeat unit
—	82.5574	82.5577	C ₁₀ H ₁₅ NO ^e	
166.1228	166.128 ^b	166.1232	C ₁₀ H ₁₆ NO	
—	83.063 ^b	83.0616	C ₁₀ H ₁₆ NO ^e	
—	83.5626	83.5656	C ₁₀ H ₁₇ NO ^e	
—	224.6768	224.6810	C ₃₆ H ₄₇ N ₄ O ₃ ^e	

^a The symbols refer to those given in Table I.

^b Broad area of overlapping peaks.

^c Intensity of product E is too weak for determination.

^d One of five products appearing in the mass range from 82.0 to 82.1.

^e Doubly charged ions.

hand, nitriles can be formed by homolytic reactions and were observed in the FI-spectra of the poly-(4,4'-dipiperidylamides) with aromatic dicarboxylic acids⁵ as well as in the spectra of polyamides containing only aromatic rings.¹¹ Obviously, for the latter only homolytic reactions allow the formation of nitriles.

High Resolution Mass Spectrometry

EI and FI measurements at high resolution were used to determine the elemental composition of the thermal degradation products and to support the proposed reaction mechanisms. The results are summarized in Table II.

Complementary results are obtained from the EI and FI spectra. Whereas amines and nitriles are observed in the EI spectrum, the corresponding protonated molecules are seen in the FI spectrum. Nitriles without protonation are mostly absent in the FI spectrum.

Field Desorption Mass Spectrometry

Protonated and doubly protonated oligomers, and those attached to sodium cations, are the main degradation products observed. Their *m/z* values and relative abundances are given in Table III. The relative abundances are the average of all scans recorded. The spectrum for nylon 6.10 is shown in Figure 3 and represents a typical spectrum of the nylon samples except nylon 6.6 and

TABLE III
Field Desorption Mass Spectrometry of Aliphatic Polyamides: m/z (Relative Abundance)

Type	n	Nylon 6.6	Nylon 6.9	Nylon 6.10	Nylon 6.12	Nylon 12.6	Nylon 12.10	Nylon 12.12
$[M_n + H]^+$	1	227(1)	269(1)	283(1)	311(8)	311(10)	367(2)	394(1)
	2	453(53)	537(16)	565(51)	621(36)	621(59)	733(13)	789(41)
	3	679(85)	805(11)	847(70)	931(53)	931(56)	1099(20)	1183(29)
	4	905(100)	1073(13)	1129(55)	1241(39)	1241(100)	1465(15)	1577(22)
	5	1131(33)	1341(9)	1411(19)	1551(17)	1551(85)	1831(3)	1971(2)
	6	1357(11)	1609(2)	1693(9)	1861(4)	1861(9)		
	7	1583(4)	1877(1)					
$[M_n + Na]^+$	1	249(0)	291(1)	305(1)	333(4)	333(1)	389(10)	417(11)
	2	475(13)	559(100)	587(100)	643(100)	643(5)	755(100)	811(100)
	3	701(96)	827(19)	869(15)	953(13)	953(21)	1121(29)	1205(6)
	4	927(36)	1095(1)	1151(1)	1263(1)	1263(18)	1487(4)	1599(1)
	5	1153(10)						
$[M_n + 2H]^{2+}$	1	114(1)	135(1)	142(5)	156(5)	156(6)	184(0)	198(0)
	3	340(26)	403(1)	424(20)	466(20)	466(6)	550(5)	592(45)
	5	566(32)	671(7)	706(28)	776(14)	776(33)	916(6)	986(8)
	7	792(10)	939(1)	988(6)	1086(3)	1086(8)	1282(4)	1380(4)
$[\text{dinitrile} + H]^+$	0	109(2)	151(16)	165(8)	193(5)	109(18)	165(2)	193(11)

nylon 12.6. Protonated oligomers for nylon 6.10 are seen at m/z 283, 565, 1129, 1411, 1693, and 1975. Doubly charged oligomers are also seen at m/z 141, 423, 706, and 987 for $n = 1, 3, 5$, and 7 . The low mass resolution does not allow distinction between doubly charged oligomers with $n = 2, 4, 6$, and 8 and singly charged oligomers with n from 1 to 4 from their isotopic peaks.

As shown in Table III the base peaks resulting from dimers attached to a sodium cation are commonly observed for the aliphatic nylon series except for nylon 6.6 and 12.6. Higher oligomers attached to a sodium cation can be seen

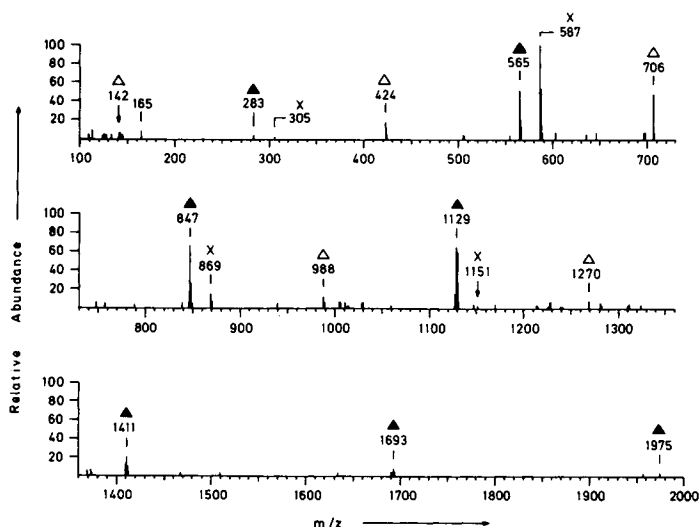


Fig. 3. FDMS of nylon 6.10: sum of all scans; (▲) protonated oligomers, (Δ) doubly protonated oligomers, (X) oligomers attached to a sodium cation.

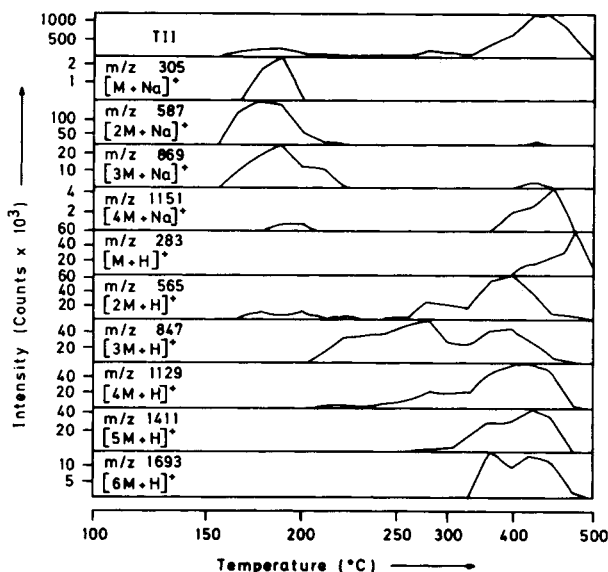


Fig. 4. FDMS of nylon 6,10: temperature dependence of the integrated ion counts, the formation of protonated oligomers, and of oligomers attached to a sodium cation.

as well, but with much lower abundances. Even traces of sodium salts present in the authentic polymer preparation allow the formation of these FD signals. They are formed in the low temperature range before evolution of any other products is observed. Figure 4 shows the total count of ions reaching the detector of the mass spectrometer. Additionally, the temperature dependence of the formation for protonated oligomers and those attached to a sodium cation is shown. The formation of cationized oligomers at lower temperatures indicates, as expected from the FI results, the presence of volatile oligomers in the polymer samples. It is noteworthy that in the FD spectra only small amounts of monomers are seen, whereas monomers were the predominantly formed products in the low temperature range under the FI conditions. Evidently, monomers may dimerize under FD conditions and form very stable complexes with sodium cations. The dimer is much preferred for nearly all nylon samples measured, except for nylon 6.6 and 12.6, where the higher abundant signals are due to the trimer. The ring size of cyclic oligomers is expected to be associated significantly with the stability of these sodium complexes. Evidently, these products are formed from monomers or oligomers present in the polymer, as they are detected in the FI mode. It has been shown that most of the oligomers formed by pyrolysis of nylons are cyclic.² As cyclic ligands are favorable for metal complexes, open chain degradation products attached to a sodium cation are only seen at very low abundances.

In the temperature range above 400°C, where the main thermal degradation occurs, the amounts of sodium containing products are very small with protonated and doubly charged oligomers being predominantly formed. Several additional products such as diamines, diamides and dicarboxylic acids are observed at low abundance. Dinitriles are formed from the dicarboxylic acid

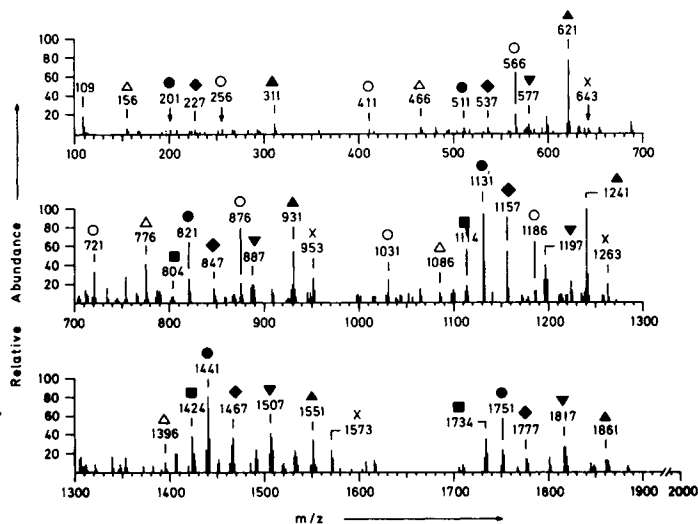


Fig. 5. FDMS of nylon 12.6: sum of all spectra. (▲) protonated oligomers, (Δ) doubly protonated oligomers, (X) oligomers attached to a sodium cation, (●) protonated diamines, (○) doubly protonated diamines, (◆) $[M_n - 83]^+$, (▼) $[M_n - 43]^+$, (■) $[M_n - 126]^+$.

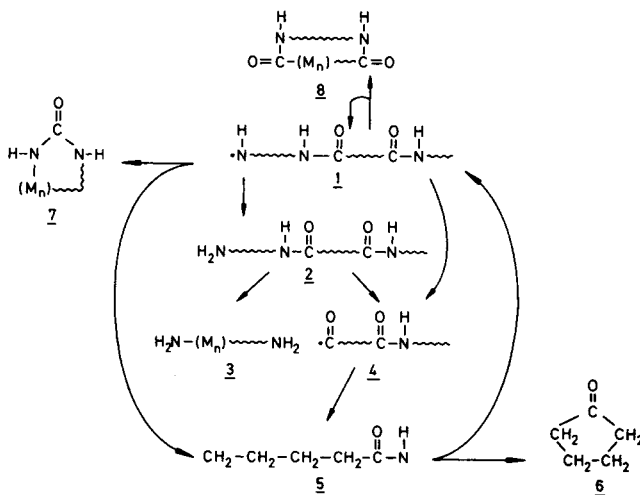
unit of the polymers, but, in contrast to any other products, no corresponding series with additional polymer repeating units are seen.

The FD spectrum of nylon 12.6, which differs greatly from those of the other samples without adipic acid subunits, is shown in Figure 5. Compared to other spectra, many additional peaks are observed with similar heights to the oligomer peaks. Protonated oligomers are seen at m/z 311, 621, 931, 1241, 1551, and 1861, and doubly charged oligomers appear at m/z 156, 466, 776, and 1086. The abundance of oligomers attached to a sodium cation is much lower than that observed in the spectra of the other nylon samples.

The higher members of the ion series $[M_n - 109]^+$ appear partially in very high abundances at m/z 201, 511, 821, 1131, 1441, and 1751. These products can be assigned to protonated diamines. The corresponding doubly protonated diamines are observed at m/z 256, 411, 566, 721, 876, 1031, and 1186. Protonated monoamines (type C in Table I) are observed at m/z 494, 804, 1114, 1424, and 1734. Protonated cyclic urea derivatives may be assigned to the series $[M_n - 83]^+$ at m/z 227, 537, 847, 1157, 1467, and 1777. Further ion series $[M_n - 43]^+$ resulting from elimination of an amide bond are observed as with the FI spectra.

Protonated oligomers and oligomers attached to a sodium cation are the main products observed in the FD spectrum of nylon 6.6. Similar to nylon 12.6, ion series indicating protonated as well as doubly protonated diamines are seen, but with lower relative abundance. As the series $[M_n - 43]^+$ and $[M_n - 83]^+$ are common to both polymers, it becomes obvious that the formation is mainly influenced by the diacid subunit and is not seriously effected by the diamine unit.

Previously, nylon 6.6 has already been investigated by FDMS.⁴ There, instead of protonated products, the corresponding products attached to a



Scheme 3. Possible degradation pathways for polyamides containing adipic acid subunits.

sodium cation were predominantly formed, as sodium chloride was added to promote cationization. The series $[(M_n - 110) + \text{Na}]^+$, $[(M_n - 84) + \text{Na}]^+$, and $[(M_n - 44) + \text{Na}]^+$ were observed which correspond to the ion series $[M_n - 109]^+$, $[M_n - 83]^+$ and $[M_n - 43]^+$ found in the FD spectra investigated in the present study.

The degradation behavior can be rationalized by the radical chain mechanism given in Scheme 3. A homolytic scission of an amide bond yields a $\text{R}-\text{NH}^\cdot$ and $\text{R}'-\text{CO}^\cdot$ radical. Hydrogen abstraction of the $\text{R}-\text{NH}^\cdot$ radical leads to an amine end group 2. A second homolytic scission of an amide bond is necessary to form diamines 3. The remaining carbonyl radical 4 loses carbon monoxide, and the alkyl radical formed will regenerate the starting radical 1 after elimination of cyclopentanone. This radical is also regenerated after formation of cyclic oligomers 8. The same type of chain reaction may operate in the formation of cyclic oligomers as with the other nylon samples. Another reaction pathway is the formation of cyclic urea derivatives combined with the formation of an alkyl radical type 5. The homolytic cleavage of amide bonds must be favorable in the thermal degradation of the nylon samples 6.6 and 12.6, as many diamines are formed involving two cleavages of this type. Hydrolysis of the amide bonds on a large scale forming amines can be excluded as mass signals assigned to dicarboxylic acids or anhydrides are not found in any significant amount. It should be noted that the polymer forming large amounts of diamines yields the lowest amounts of oligomers attached to sodium cations.

FD spectra similar to those observed for nylon 12.6 were obtained from aliphatic poly-(4,4'-dipiperidylamides).⁵ The main degradation products contain two 4-piperidyl end groups corresponding to the diamines formed from nylon 12.6. Whereas oligomers were found in large amounts from the polymer containing succinic acid units, only extremely low amounts were seen in the spectra from the polymers containing adipic acid units. Here, a similar reaction pathway to that in Scheme 3 may occur. In contrast to the linear

polymers which are investigated in this paper, a general preference of diamine formation over oligomer formation is found for branched dipiperidylamides. This fact may contribute to the easier formation of cyclic products from primary amine radicals than from secondary amine radicals.

CONCLUSIONS

Direct pyrolysis and soft ionization mass spectrometry allows the detection of molecular ions of high-mass thermal degradation products. Generally, many series of degradation products differing by the mass units corresponding to intact repeating units of the polymers are seen in the FI spectra and give direct structural information. These high-mass signals also indicate that the bond cleavages are occurring randomly along the polymer chain. The main degradation pathway is strongly dependent on the diacidic subunit. For all samples without adipic acid subunits the same mechanisms are operative to those found for flash pyrolysis. Large amounts of nitriles and dinitriles are formed. In addition to a six-membered transition state suggested for nitrile formation, a similar six-membered transition state is suggested in order to explain the cleavage between the α - and β -methylene group of the diacidic subunit. On the other hand, for the adipic acid derivatives nylon 6.6 and nylon 12.6, the formation of amines is preferred to that of nitriles. Thus, the mechanism suggested may be favorable for polymers containing this diacidic subunit.

The temperature resolution in the time/temperature-resolved FI mass spectra allows a clear distinction between cyclic oligomers present in the original polymer and oligomers formed by thermal degradation of the polymer chain.

The comparison of the EI and FI high resolution data proves the formation of amines and nitriles. The formation of the corresponding protonated products is induced by FI as these products can be assumed to be absent in the primary thermal degradation process.

In the FD mode, predominantly protonated and doubly protonated oligomers are formed as expected for soft ionization from an adsorbed polymer layer on the emitter surface. At low temperatures, oligomers attached to a sodium cation are observed, accompanied by traces of protonated oligomers. These oligomers can be assigned to cyclic oligomers already present in the polymer. At higher temperatures, protonated and doubly protonated oligomers are observed, accompanied by traces of oligomers attached to a sodium cation, and arise from thermal degradation of the polymer chain.

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