

Pyrolysis-Field Ionization Mass Spectrometry of Polyamide Copolymers and Blends

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Synopsis

Nylon foils of PA 6, PA 66, PA 69, PA 12, the copolymer PA 666, and nine blends based on these polyamides have been investigated by in-source pyrolysis (Py)-field ionization mass spectrometry (FIMS). These polymers and blends can be distinguished by characteristic molecular ions of oligomers, protonated amines and nitriles, and products terminated by olefinic end groups. Series of ions are formed differing in the number of additional monomeric units. Thus, polymers containing different chemical subunits were easily distinguished from each other in the spectra of the blends. Mass signals, only expected for copolymers, were found in the integrated blend spectra, indicating that amide exchange reactions occur under the experimental conditions employed. This observation was confirmed by pyrolysis of mixtures of pure polymers in the same crucible and under the same experimental conditions. Hence, the distinction by Py-MS alone between blends and copolymers with an identical averaged number of identical chemical subunits is not possible.

INTRODUCTION

Pyrolysis (Py)-mass spectrometry (MS) is a powerful tool for the investigation of polymers.¹⁻³ Using field ionization (FI) as the soft ionization mode, molecular ions of the thermal degradation products are predominantly formed.^{3,4} The lack of strong mass spectrometric fragmentation facilitates the detection of the specific thermal degradation products, which are formed as complex mixtures on pyrolyzing the polymers.

Recently, Py-FIMS was successfully employed for the investigations of linear aromatic⁵ and aliphatic⁶ polyamides, crosslinked epoxy resins,⁷ uncured rubbers,⁸ and rubber vulcanizates.⁹ The time-temperature-resolution allowed the distinction between residual monomers^{6,7} from polymer pyrolyzates. Furthermore, rubbers containing high amounts of organic additives were easily determined.^{8,9} Without time-temperature-resolved MS, significant mass signals due to the polymer backbone were mostly obscured by abundant signals due to the additives.^{8,9}

The degradation pathway for diamine-dicarboxylic acid-type polyamides was found to be strongly dependent on the number of methylene groups in the dicarboxylic acid subunit.⁶ Whereas oligomers and protonated nitriles were found for PA 69 and most other samples, little nitrile formation was observed for polymers containing adipic acid subunits. In contrast to the other samples, high amounts of protonated amines as well as oligomers were formed from PA 66. Using field desorption (FD) mass spectrometry, predominantly

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oligomers and oligomers attached to a sodium cation are formed from PA 69,⁶ PA 6, PA 12, and PA 66.¹⁰

The main thermal degradation product which has been observed by flash pyrolysis GC/MS of PA 6 was the monomer.¹¹ In addition, smaller amounts of nitriles were found. For PA 12, the corresponding nitriles formed the main degradation products. Likewise, large amounts of nitriles, and especially dinitriles, were obtained from PA 69 and other diamine–dicarboxylic acid-type polyamides except those containing adipic acid subunits. In contrast, cyclopentanone was the main pyrolysis product of PA 66 and PA 126, with little nitrile formation. Moreover, derivatives of cyclopentanone were recently determined by direct chemical ionization mass spectrometry of PA 66.¹²

In the present paper, polyamide foils of pure polymers and blends are investigated. The components of the PAs are the ω -aminoacid-type polymers PA 6 and PA 12, the diamine–dicarboxylic acid-type polymers PA 66 and PA 69, and PA 666, which is the copolymer of PA 6 and PA 66. The aim of the study was the identification of the polyamide components in the blends and the distinction between copolymers and blends.

EXPERIMENTAL

The Py–FIMS experiments were performed using the modified direct introduction system of a Finnigan MAT double-focusing mass spectrometer.¹³ The samples were heated from 50 to 750°C in high vacuum at about 10^{-3} PA with a heating rate of 1.2°C s^{-1} . The thermal degradation products were ionized at +8 kV emitter potential; the counter electrode was at –3 kV. All mass spectra were recorded electrically and averaged by the Finnigan SS 200 data system. Further experimental details have been described.^{14,15}

The polyamide foils were prepared by M. Martin, Fachhochschule Frese-
nius, from the commercially available polymers listed in Table I.¹⁶

RESULTS AND DISCUSSION

Pure Polymers

The main mass signals observed in Py–FIMS for PA 6, PA 66, and for the copolymer of these two polyamides, PA 666, are listed and tentatively interpreted in Table II. Relative abundances of the FI ions and assigned structures are included. Many mass signals are common to the three samples and are attributed to oligomers, protonated amines, and products terminated by olefinic end groups. Oligomers appear as $[\text{M}_n]^{++}$ and $[\text{M}_n + \text{H}]^+$ ions, which are typical of various polyamides.⁶ In addition, PA 666 shows abundant mass signals which are absent in the spectra of the two homopolymers PA 6 and PA 66. These mass signals belong to products containing the PA 6 as well as PA 66 subunits. As the molecular weight of the monomeric unit of PA 6 is half that of PA 66, no distinction by low and high mass resolution is possible between one additional subunit of PA 66 or two additional subunits of PA 6 involved in the formation of the homologous series differing by 113 mass units in the spectrum of PA 666.

The spectra of the two PA 666 copolymers contain the same mass signals, but with very different relative abundances. Ultramid 6A forms high abun-

TABLE I
Commercial Polyamides¹³ Investigated by Py-FIMS

Polymer type	Trade name	Manufacturer	Formula subunit	Mol wt subunit
PA 66	Ultramid A4	BASF, Ludwigshafen, F. R. G.	$(-\text{NH}-(\text{CH}_2)_6\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO}-)_n$	226
PA 6	Ultramid B4	BASF, Ludwigshafen, F. R. G.	$(-\text{NH}-(\text{CH}_2)_5-\text{CO}-)_n$	113
PA 666	Ultramid 6A	BASF, Ludwigshafen, F. R. G.	PA 6 and PA 66 subunits	
PA 666	Novamid 2030	Mitsubishi, Tokyo, Japan	PA 6 and PA 66 subunits	
PA 69	Ultramid KR 4609	BASF, Ludwigshafen, F. R. G.	$(-\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{CO}-(\text{CH}_2)_7-\text{CO}-)_n$	268
PA 12	Grilamid L25	Emser Werke AG, Switzerland	$(-\text{NH}-(\text{CH}_2)_{11}-\text{CO}-)_n$	197

TABLE II
Mass Signals and Structures Assigned for Thermal Degradation Products of the Polymers PA 6, PA 66, and PA 666

m/z	Relative abundance				Proposed structure ^a	
	Ultramid A4	Ultramid B4	Ultramid 6A	Novamid 2030		
113	5	100	100	100	Oligomers	
226	23	16	13	18		
339	—	26	34	20		
452	98	67	54	55		
565	—	72	68	42		
678	14	15	20	11		
183	4	6	4	5		
296	—	1	4	1		
409	33	7	15	4		
522	—	20	38	6		
635	63	12	74	19		
748	—	1	3	2		
96	—	16	4	16		
209	4	14	3	7		
322	—	20	4	7		
435	11	31	8	12		
548	—	63	10	36		
661	10	44	—	26		

117	5	—	4	1	
230	—	—	10	—	
343	51	—	32	1	
456	—	1	74	6	
569	100	—	100	6	
682	—	—	6	—	
100	3	—	4	1	
213	—	—	2	2	
326	8	—	6	3	
439	—	1	25	8	
552	46	—	65	23	
665	—	—	55	—	
195	—	1	2	2	
308	1	4	3	2	
421	—	1	2	4	
534	—	2	8	12	
647	—	2	22	28	
760	—	—	4	7	

^aThese structures are due to the basic subunits. The higher mass signals correspond to products with additional PA 6 or/and PA 66 subunits.

^bThese structures are formed with PA 66 subunits only.

^cThese structures are formed with PA 6 subunits only.

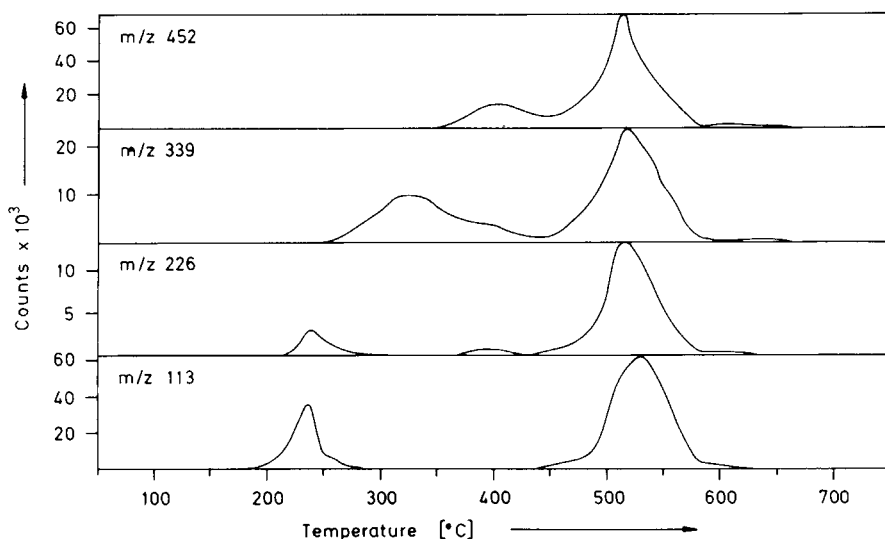


Fig. 1. Temperature dependence of the formation of the monomer and oligomers from Ultramid 6A.

dant mass signals common to PA 66. The mass signals observed for PA 6 are seen with moderate abundances. These results suggest a copolymer containing more subunits of PA 66 than PA 6. Large amounts of products containing PA 6 as well as PA 66 subunits are formed, especially at m/z 439, 456, 647, and 655 (see Table II), indicating the presence of large quantities of both homopolymer components. In contrast, Novamid 2030 shows high abundant mass signals typical of PA 6, indicating that this subunit is the main component of this copolymer. The abundances of mass signals related to PA 66 or to products containing both PA 6 and PA 66 subunits are very much lower than observed for Ultramid 6A. The ion at m/z 569, which forms the base peak of the PA 66 Ultramid A4 and the PA 666 Ultramid 6A, appears only with 6% relative abundance. As the hexamethylene-diamine subunit of PA 66 is required for the formation of this mass signal, the small amount of PA 66 subunits is obvious.

Free monomers and oligomers are present in the polymer samples. As a typical example, the temperature dependence of the oligomer formation is shown for Ultramid 6A in Figure 1. With increasing temperature, the volatile oligomers appear one after another with increasing number of subunits. Using temperature resolved Py-FIMS, these oligomers can be assigned to oligomers already present in the original polymers, or to those formed in the preparation of the foils, respectively. A similar contribution of volatile oligomers was found for Ultramid B4. For Novamid 2030, the amounts of oligomers formed at temperatures below 450°C are lower. At temperatures above 450°C, all ions due to oligomers are formed at the same time indicating polymer degradation as origin of oligomer formation.

The spectra of PA 69 and PA 12 differ strongly from those mentioned above. As observed for PA 6 and PA 66, oligomer formation takes place. In contrast to PA 66, abundant signals due to protonated diamines are absent for

PA 69. On the other hand, nitriles are observed with high abundance, whereas the formation of amines is very low. Recently, it has been shown that under the experimental conditions employed the degradation mechanisms are different for aliphatic polyamides containing adipic acid subunits, and those which do not.⁶ In agreement with these investigations, the degradation products found for PA 69 are oligomers (m/z 268, 536, 804, relative abundance 33, 100, 3%, respectively) and protonated dinitriles (m/z 151, 419, 687, relative abundance 17, 23, 37%, respectively). Further, products are observed which are terminated by one protonated nitrile end group and one olefinic endgroup (m/z 251, 519, 787, relative abundance 23, 26, 13%, respectively).

The spectrum of PA 12 shows oligomers (m/z 197, 394, 591, 788, relative abundance 20, 100, 58, 72%, respectively), accompanied by mass signals of similar abundance which appear one mass unit higher. Elimination of water yields protonated nitriles (m/z 377, 574, 771, relative abundance 10, 11, 43%, respectively). In addition, random splitting of the aliphatic chain occurs forming ion series differing by 14 mass units. The relative abundance of these products is below 5% up to m/z 600, increases to 10% in the mass range about 600–700 and to 20% in the mass range from 700 to 850 daltons.

Blends of PA 6, PA 66, and PA 666

The relative abundances and mass signals typical for PA 6, PA 66, and PA 666 are listed for each sample in Table III. In general, mass signals observed with similar relative abundances in both PA 6 and PA 66 homopolymer spectra are omitted. The blends of PA 6 and PA 66 show abundant mass signals which are absent in both spectra of the homopolymers and are assigned to thermal degradation products which are only expected for a copolymer of PA 6 and PA 66. Hence, amide exchange reactions must occur under the experimental conditions employed. In order to prove this assumption, a 1:1 blend of Ultramid A4 and Ultramid B4 was pyrolyzed in the same crucible under standard conditions. Here, mass signals absent in both of the single spectra are observed. The relative abundances of mass signals only expected for copolymers are lower than from the blends, probably since both polymers were used as two bulky pieces without any cutting and mixing. Therefore, the distinction between a blend and a copolymer with the same number of equal subunits is not possible by this analytical method.

The amide exchange reactions responsible for the formation of mass signals due to copolymers have already been observed by pyrolyzing alternating aliphatic-aromatic copolyamides consisting of ω -aminobutyric acid and *p*-aminobenzoic acid units.^{17,18} At temperatures above 250°C, butyrolactam was split from the polymer chain followed by the recombination of amide bonds between two aromatic units. Whereas mass signals due to the alternating structure were found on direct pyrolysis, a spectrum similar to polyaminobenzoic acid was obtained by prior heating at 360°C. Here, the opposite effect to that observed in this study takes place, mass signals due to a homopolymer are formed from an alternating copolymer. Obviously, the same reaction mechanism is responsible for both effects.

The spectra of the two blends 1 and 2, consisting of PA 6 and PA 66, differ in the relative abundances of the common mass signals. Mass signals typical of

TABLE III
Mass Signals Observed for Blends of PA 6, PA 66, and PA 666

<i>m/z</i>	Relative abundances ^a				Proposed structure
	Blend 1	Blend 2	Blend 3	Blend 4	
343	11	32	2	12	Typical mass signals for PA 66
569	27	95	—	26	
326	6	12	—	8	Typical mass signals for PA 6
552	42	79	13	67	
113	84	51	100	86	
339	24	22	36	26	
565	76	75	42	85	
522	17	26	15	10	Typical mass signals for PA 666 Copolymer
322	8	8	15	10	
548	47	41	46	75	
456	16	26	7	20	
534	12	18	14	27	
647	39	34	11	52	
760	23	23	7	19	
439	18	21	9	20	
665	36	41	4	16	

^aBlend 1: 30% Ultramid A4, 70% Ultramid B4. Blend 2: 60% Ultramid A4, 40% Ultramid B4. Blend 3: 40% Ultramid B4, 60% Novamid 2030. Blend 4: 30% Ultramid A4, 30% Ultramid B4, 40% Novamid 2030.

PA 66 are larger for blend 2 corresponding to the higher PA 66 content. In contrast, the monomer of PA 6 is more abundant in the spectrum of blend 1. Further mass signals typical of PA 6 and PA 666 appear with similar relative abundances for both blends. Mass signals listed as typical of PA 6 may also be formed from PA 666, for instance, the trimer of PA 6 subunits appears at the same *m/z* value as the mixed oligomer containing one subunit of each polymer. Nevertheless, comparing the ratios of the sum of the relative abundances for mass signals related to PA 6 to the sum of the relative abundances related to PA 66, the higher content of PA 6 in blend 1 and the higher content of PA 66 in blend 2 is obvious.


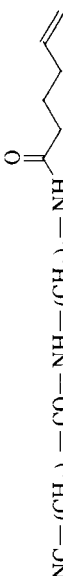

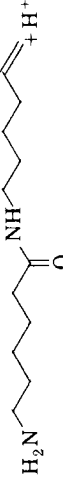

As Novamid 2030 contains mainly PA 6 subunits, the averaged number of PA 6 and PA 66 subunits is very similar between blends 1 and 4. Indeed, the mass spectra of both blends are really very similar. Blend 3 contains mainly PA 6 subunits leading to a spectrum of predominantly PA 6 related mass signals. Low abundant mass signals related to a copolymer and very low abundant mass signals related to PA 66 are also observed.

Blend of PA 666 and PA 12

Amide exchange reactions are observed on pyrolyzing a blend of 20% Grilamid L25 and 80% Ultramid 6A. In addition to mass signals present in the spectra of both components, oligomers containing one unit PA 12 and some PA 6 units are observed at *m/z* 310, 423, 536, 649, and 762 with relative

TABLE IV
Thermal Degradation Products from a Blend of PA 6 and PA 69 m/z (Relative Abundance)

Additional monomeric units PA 6	Additional monomeric units PA 69			Proposed structure
	0	1	2	
0				Oligomers NC—(CH ₂) ₆ —CN + H ⁺
1	113 (77)	268 (4)	536 (16)	
2	226 (10)	381 (6)	649 (10)	
3	339 (16)	494 (12)	762 (5)	
4	452 (50)	607 (19)		
5	565 (48)	720 (2)		
6	678 (15)			
0	151 (1)	419 (3)	687 (12)	
1	264 (2)	532 (5)	800 (—)	
2	377 (2)	645 (19)		
3	490 (8)	758 (12)		
4	603 (25)	871 (—)		
5	716 (14)			

0	96 (14)	364 (2)	632 (13)	
1	209 (10)	477 (5)	745 (9)	$\text{NC}-(\text{CH}_2)_7-\text{CO}-\text{NH}-(\text{CH}_2)_6-\text{NH}^+$
2	322 (10)	590 (30)	858 (—)	
3	435 (20)	703 (23)		
4	548 (32)	816 (8)		
5	661 (18)			
0	195 (2)	463 (4)	731 (18)	
1	308 (2)	576 (8)	844 (2)	
2	421 (5)	689 (5)		
3	534 (12)	802 (1)		
4	647 (17)			
5	760 (8)			
0	213 (1)	481 (8)	749 (8)	
1	326 (1)	594 (14)	862 (—)	
2	439 (4)	707 (3)		
3	552 (10)	820 (—)		
4	665 (1)			
5	778 (3)			

abundances of 3, 6, 14, 33, and 12%, respectively. As noted above, it is impossible to distinguish between one additional subunit of PA 66 and two additional subunits of PA 6. In addition, according to the products listed in Table II at m/z 409, 522, and 552, the corresponding products containing one additional subunit PA 12 are observed at m/z 606, 719, and 749. The relative abundances are 24, 16, and 13%, respectively. Furthermore, high abundant mass signals at m/z 343 and 569 are related to PA 666. The corresponding products containing one additional subunit of PA 12 are observed at m/z 540 and 653 with 9% relative abundance.

Similar results are obtained from the blend of 20% Grilamid L25 and 80% Novamid 2030. The spectrum shows mass signals seen in both single-component spectra, the relative abundance of the base peak for PA 12 at m/z 394 is 24%. Mixed oligomers are seen as with the Grilamid L25-Ultramid 6A blend. Both PA 666-PA 12 blends can be distinguished by the differences already observed for both PA 666 components.

Blend of PA 6 and PA 12

Similar results to those observed for the PA 12/PA 666 blend, are obtained from the PA 12/PA 6 blend of 20% Grilamid L25 and 80% Ultramid B4. The relative abundance of the peak at m/z 394, which forms the base peak of PA 12, is 18%. Mixed oligomers containing one unit PA 12 and some PA 6 units are seen at m/z 310, 423, 536, and 649 with relative abundances of 4, 4, 7, and 9%, respectively. Oligomers containing two PA 12 subunits appear at m/z 507, 620, and 733 with relative abundances of 11, 17, and 4%, respectively.

Blend of PA 6, PA 666, and PA 12

The blend of 30% Ultramid B4, 40% Grilamid L25, and 40% Novamid 2030 yields oligomers of PA 6 containing one unit of PA 12 at m/z 310, 423, 546, and 649 with relative abundances of 7, 6, 18, and 17%, respectively. The ion m/z 606, already seen in the PA 666/PA 12 blend, appears with 16% relative abundance. Low amounts of the PA 66 subunit are indicated by the formation of the peak at m/z 569, which forms the base peak of PA 66 and is assigned to a protonated diamine. The relative abundance of this peak in the blend spectrum is only 3%, indicating the low amount of PA 66 subunits.

Blend of PA 6 and PA 69

In addition to the mass signals due to the single components, the blend of 30% Ultramid KR 4609 and 70% Ultramid B4 shows mixed oligomers, which are included in Table IV. As with PA 69, products terminated with olefinic end groups and protonated nitriles are formed. As amide exchange reactions occur, several different series of signals are formed containing additional monomeric units of both components (Table IV).

CONCLUSIONS

The reliable identification of different homopolyamides is readily performed by direct Py-FIMS. The time/temperature resolution allows the distinction between volatile oligomers already present in the polymer and those formed from thermal degradation of the polymer backbone. Pyrolysis of two homopolymers jointly in the same crucible yields additional signals, which are absent in both single component spectra. Thus, intermolecular amide exchange reactions occur under the experimental conditions employed which lead to signals expected for copolymers only. Hence, a blend of PA 6 and PA 66 cannot be distinguished from a PA 666 sample with the same average number of identical chemical subunits. However, the simultaneous presence of different polyamide subunits can easily be detected.

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References

1. H.-R. Schulten and R. P. Lattimer, *Mass Spectrom. Rev.*, **3**, 231 (1984).
2. S. Foti and G. Montaudo, *Analysis of Polymer Systems*, L. S. Bark and N. S. Allen, Eds., Applied Science, London, 1982, Chap. 5, p. 109.
3. D. O. Hummel, H.-D. Schüddemage, and K. Rübenacker, *Polymer Spectroscopy*, D. O. Hummel, Ed., Verlag Chemie, Weinheim, 1974.
4. H.-R. Schulten and J. M. Halket, *Org. Mass Spectrom.*, **21**, 2343 (1986).
5. H.-R. Schulten, B. Plage, H. Ohtani, and S. Tsuge, *Angew. Makromol. Chem.*, **155**, 1 (1987).
6. H.-R. Schulten and B. Plage, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 2381 (1988).
7. B. Plage and H.-R. Schulten, *Macromolecules*, **21** (1989), to appear.
8. R. P. Lattimer, R. E. Harris, C. K. Rhee, and H.-R. Schulten, *Rubber Chem. Technol.*, **61**, 639 (1988).
9. H.-R. Schulten, B. Plage, and R. P. Lattimer, *Rubber Chem. Technol.*, to appear.
10. U. Bahr, I. Lüderwald, R. Müller, and H.-R. Schulten, *Angew. Makromol. Chem.*, **120**, 163 (1984).
11. H. Ohtani, T. Nagaya, Y. Sugimura, and S. Tsuge, *J. Anal. Appl. Pyrolysis*, **4**, 117 (1982).
12. A. Ballistreri, D. Garozzo, M. Giuffrida, and G. Montaudo, *Macromolecules*, **20**, 2991 (1987).
13. H.-R. Schulten, N. Simmleit, and R. Müller, *Anal. Chem.*, **59**, 2903 (1987).
14. H.-R. Schulten, *J. Anal. Appl. Pyrolysis*, **12**, 149 (1987) and references cited therein.
15. H.-R. Schulten, N. Simmleit, and R. Müller, *Anal. Chem.*, **59**, 2903 (1987).
16. M. Martin, Diploma thesis, Fachhochschule Fresenius, Wiesbaden, 1987.
17. H. R. Kricheldorf and E. Leppert, *Makromol. Chem.*, **175**, 1731 (1974).
18. I. Lüderwald and H. R. Kricheldorf, *Angew. Makromol. Chem.*, **56**, 173 (1976).

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