Analysis of Nylon-6 by Thermal Desorption and Pyrolysis Combined with DART-MS (TDP/DART-MS) and Py-GC/MS

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Introduction

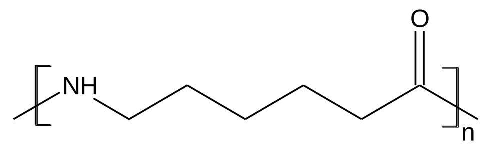
- In the field of polymer chemistry, especially for polymer characterization, pyrolysis (Py)-GC/MS is widely recognized as one of the useful analysis methods.
- Thermal Desorption and Pyrolysis combined with Direct Analysis in Real Time-Mass Spectrometry (TDP/DART-MS) is useful method for polymer analysis[1, 2].
- Additionally, in recent our experiments, we have shown that TDP/DART-MS is also capable of detecting not only low molecular weight pyrolysis products but also high molecular weight oligomeric fragments[1].

The purpose of this work :

To compare TDP/DART-MS and Py-GC/MS for the analysis of nylon-6.

Experimental

- Material : Nylon-6 (SIGMA-ALDRICH)
- Analytical methods : Py-GC/MS and TDP/DART-MS



Nylon-6
$[C_6H_{11}NO]_n$
$Mw_{(repeat\ unit)}$ 113

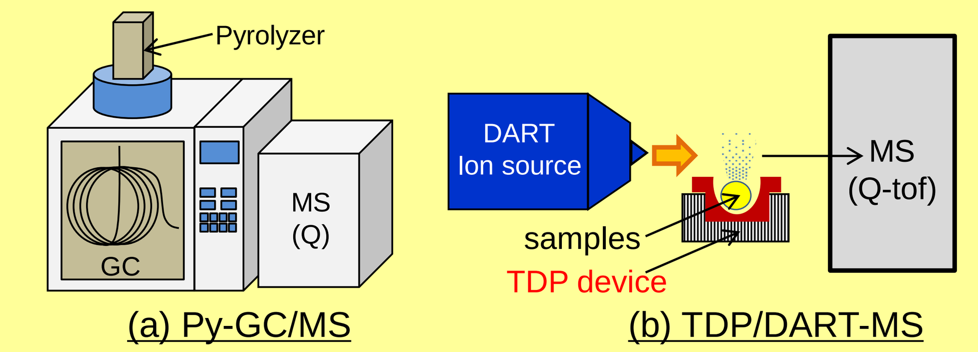


Fig.1 Analytical systems

Table 1 Analytical conditions

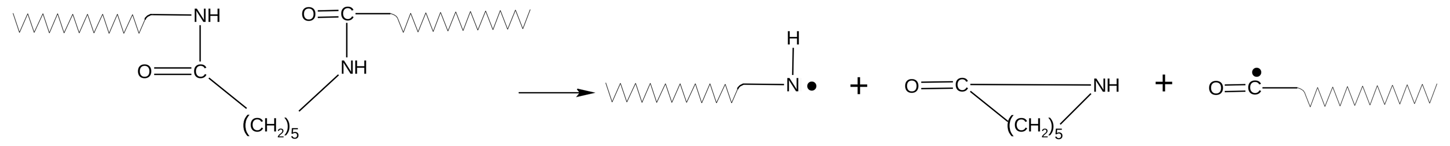
Py-GC/MS	TDP/DART-MS
Pyrolyzer: PY-3030D (Frontier Lab) GC/MS: 7890GC/5977MSD (Agilent)	TDP device: ionRocket (BioChromato) Ion source: DART-SVP (IonSense) MS Spec.: micrOTOF QIII（Bruker）
Pyrolyzer: 600 ℃ Column: Frontire lab UA-5 30 m x 0.25 mm id, 0.25 um Carrier: He, 1.5 ml/min Oven: 40 ℃ for 2 min 20 ℃/min to 320 ℃ 320 ℃ for 13 min Total 29 min Injection: Split 100:1, 320 ℃ Detector: EI Ionization MSD source at 300 ℃ Quadrupole Scan range *m/z* 29-600 Sample: ca. 0.2 mg	TDP device: RT for 1 min 100 ℃/min to 600 ℃ 600 ℃ for 1 min Total 8 min Carrier: (Air) Detector: DART Ionization Ionization gas He, 400 ℃ Q-TOF Mass range *m/z* 50-2000 Sample: ca. 0.2 mg

Results and Discussion

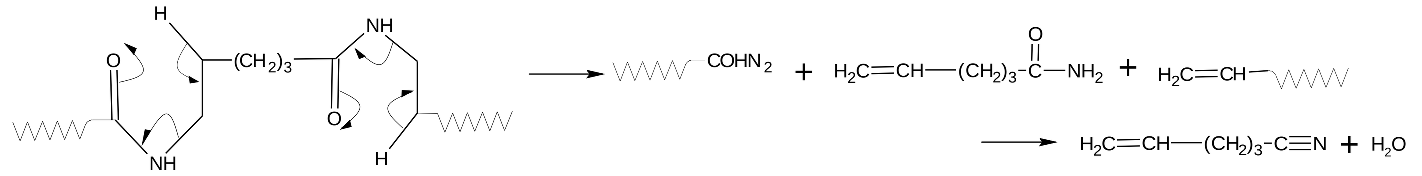
Py-GC/MS[3)]

Total ion current chromatogram (TICC) and enlarged TICC of nylon-6 using Py-GC/MS are shown in Fig.2 and Fig.3, at a pyrolysis temperature 600 ℃. 10 kinds of major pyrolysis products were observed (Table 2). The top 4 major mass spectra are shown in Fig.4.

The main product was the associated lactam, ε-caprolactam. This was caused by thermal cleavage of the C-N bonds in the backbone of the polymer chains followed by cyclization:



In addition the olefinic mononitrile compounds were formed by the dehydration reaction:



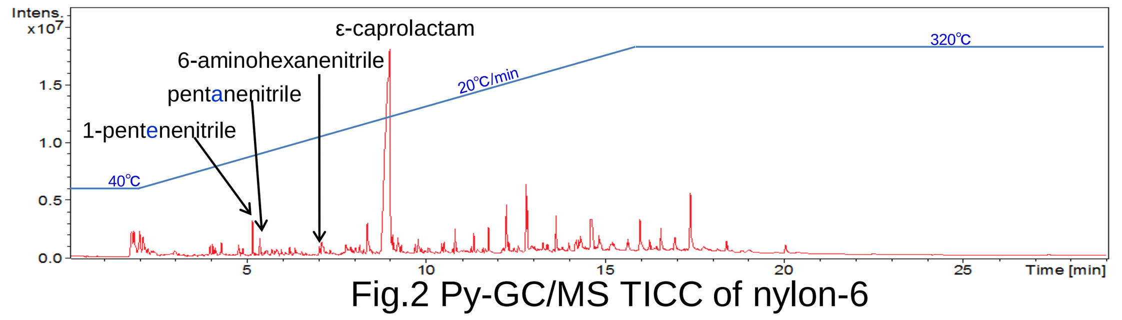


Fig.2 Py-GC/MS TICC of nylon-6

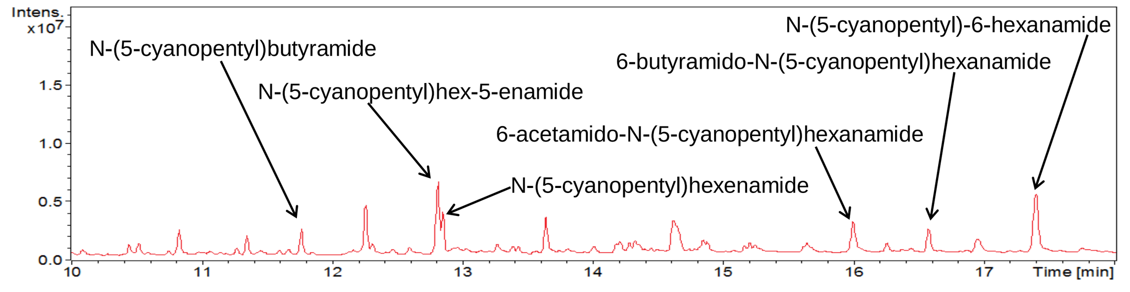


Fig.3 Enlarged Py-GC/MS TICC of nylon-6 (10-18 min)

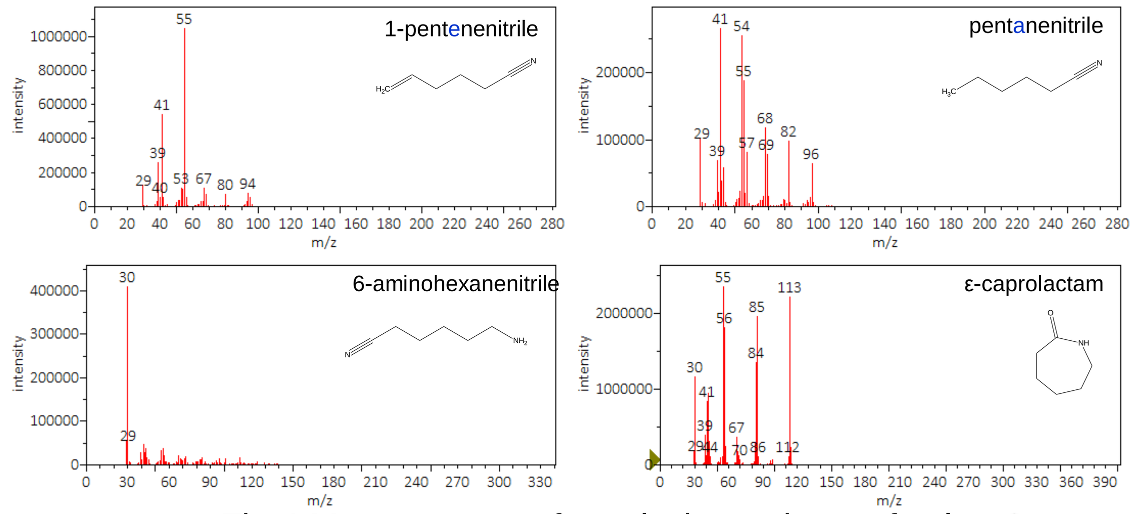


Fig.4 Mass spectra of pyrolysis products of nylon-6

Table 2 Pyrolysis products of nylon-6 observed using Py-GC/MS [4)]

Assigned compounds	Molecular Weight
1-pentenenitrile	95
pentanenitrile	97
6-aminohexanenitrile	112
ε-caprolactam	113
N-(5-cyanopentyl)butyramide	182
N-(5-cyanopentyl)hex-5-enamide	208
N-(5-cyanopentyl)hexenamide	210
6-acetamido-N-(5-cyanopentyl)hexanamide	267
6-butyramido-N-(5-cyanopentyl)hexanamide	295
N-(5-cyanopentyl)-6-hexanamide	323

TDP/DART-MS

Total ion current gram(TIC) and heat map of nylon-6 using TDP/DART-MS are shown in Fig.5 and Fig.6. With the temperature gradient heating, the thermal desorption and pyrolysis reaction were detected as change in the signal intensity. Averaged mass spectrum from 1 to 8 min (at RT to 600 ℃) was shown in Fig.7. TDP/DART-MS detected oligomeric fragments of nylon-6 which were not observed by Py-GC/MS.

Moreover, enlarged mass spectra of typical pyrolysis products using TDP/DART-MS are shown in Fig.8. As a results of TDP/DART-MS analysis, 10 kinds of major pyrolysis products observed using Py-GC/MS were also detected (Table 3).

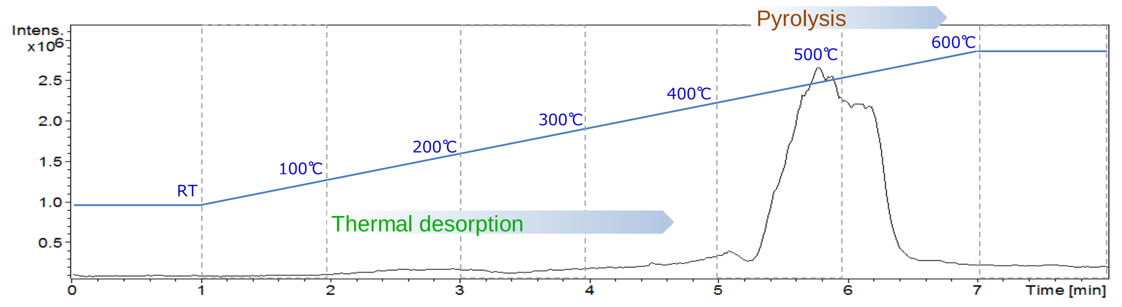


Fig.5 TDP/DRT-MS TIC of nylon-6

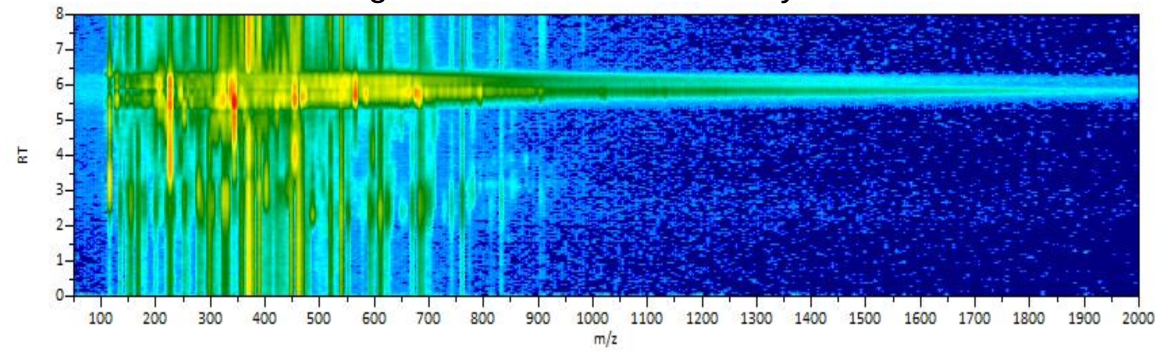


Fig.6 Heat map of nylon-6 using TDP/DART-MS

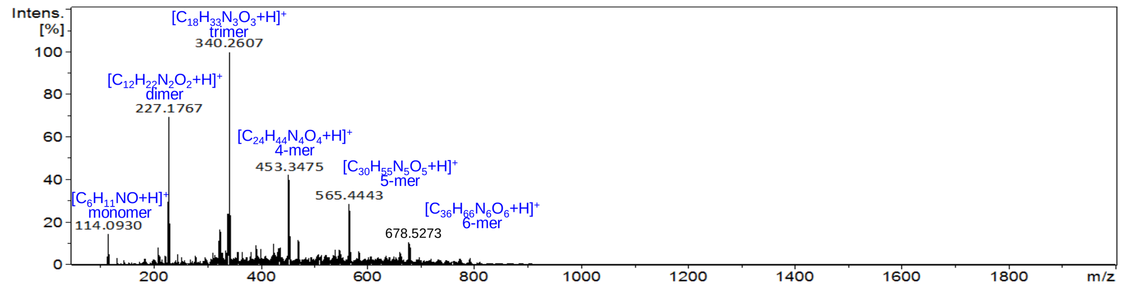


Fig.7 Averaged mass spectrum of nylon-6 using TDP/DART-MS for 1-8 min

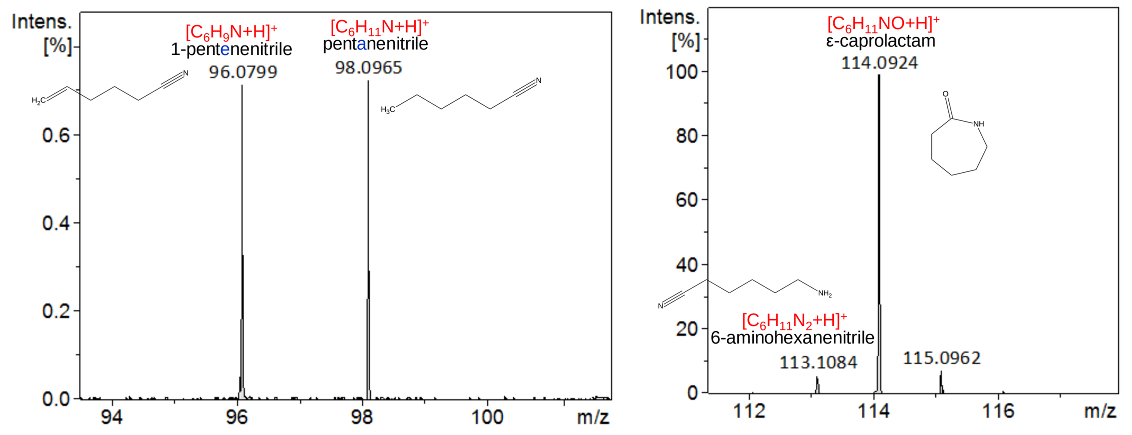


Fig.8 Enlarged averaged mass spectra for 1-8 min

Table 3 Pyrolysis products of nylon-6 observed using TDP/DART-MS

	Elemental Composition	Theoretical monoisotopic mass		Observed mass	Error (ppm)
		M	[M+H]+		
1-pentenenitrile	C6H9N	95.073499	96.081324	96.0799	9.5
pentanenitrile	C6H11N	97.089149	98.096974	98.0965	-1.1
6-aminohexanenitrile	C6H12N2	112.100048	113.107873	113.1084	-9.3
ε-caprolactam	C6H11NO	113.084064	114.091889	114.0924	-9.7
N-(5-cyanopentyl)butyramide	C10H18N2O	182.141913	183.149738	183.1517	-8.8
N-(5-cyanopentyl)hex-5-enamide	C12H20N2O	208.157563	209.165388	209.1666	-8.2
N-(5-cyanopentyl)hexenamide	C12H22N2O	210.173213	211.181038	211.1819	6.6
6-acetamido-N-(5-cyanopentyl)hexanamide	C14H25N3O2	267.194677	268.202502	268.2062	15.9
6-butyramido-N-(5-cyanopentyl)hexanamide	C16H29N3O2	295.225977	296.233802	296.2391	-19.7
N-(5-cyanopentyl)-6-hexanamide	C18H33N3O2	323.257277	324.265102	324.2468	-0.6

Table 4 Comparison Py-GC/MS with TDP/DART-MS

	Py-GC/MS	TDP/DART-MS
Comprehensibility	+-- Irreversible adsorption in the separation column, and condensation at “cold spots” such as injection port or transfer line are potential limitations.	+++ No separation column exist. No “cold spots” exist. The detection of compounds with higher boiling points or higher molecular weights are possible.
Qualitative analysis	+++ Vast spectral library is available owing to past studies. --- However, the observed pyrolysis products are often unidentified, because the analysis of EI mass spectra without a spectral library is difficult.	+-- Only a small spectral library is available. +++ However, since DART is a soft ionization technique, elemental compositions can be determined even for oligomeric pyrolysis products, which give us valuable clue to elucidate the chemical structure of unknown compounds.

Conclusion

- Py-GC/MS is widely recognized as one of the most useful analytical methods in the field of polymer chemistry. However, not only the oligomeric products are unobserved but also some compounds are unidentified using Py-GC/MS although a vast spectral library is available, because of the lack of their spectral data in the library.
- TDP/DART-MS enables the analysis of oligomeric pyrolysis products which were not observed by Py-GC/MS. Moreover, because DART ionization exclusively generates molecular ions, elemental compositions of the products can be determined.
- The combination of Py-GC/MS and TDP/DART-MS could facilitate the elucidation of the thermal decomposition of polymers and should contribute to the further development of the field of polymer chemistry.

References

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