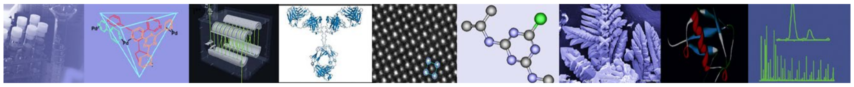


Evolved gas monitoring from PA66 by using PY-GC-HRTOFMS

Introduction

Compounds which are generated upon heating polymer materials include monomers, additives and fragments characteristic of the polymer materials. Low molecular weight compounds generated by pyrolysis and/or locally desorption are observed. The relationship between the behavior of evolved gas compounds and the heating temperature is important for understanding the chemical characteristics of polymer materials. A gas chromatograph (GC) - mass spectrometer (MS) with thermogravimetric / differential thermal analyzer (TG/DTA) or pyrolyzer (Py) is generally used to identify the thermally evolved gas compounds from polymer materials. However, GC with a low-resolution MS such as quadrupole MS (QMS) may have difficulty monitoring low molecular-weight compounds generated by heating, since the GC is not used to provide chromatographic separation and QMS has poor mass spectrometric separation in the low mass region. (For example, $N_2^{+\cdot}$, $CO^{+\cdot}$ and $C_2H_4^{+\cdot}$ are detected as the same signal of nominal mass *m/z* 28.)

We report the use of Py - GC - high resolution time-of-flight MS (HRTOFMS) for monitoring the low-molecular weight compounds generated upon heating the polymer materials. This report focuses on the generation of low molecular weight compounds near *m/z* 18, 28, 4and 4.

	Conventional method	This application method
	Py/GC/QMS	Py/GC/HRTOFMS
Identification technique	Library searching	Library searching and determination of chemical formula from accurate mass
Monitoring of low-molecular weight compounds	Very difficult without chromatographic separation	Possible by high resolution

Experimental

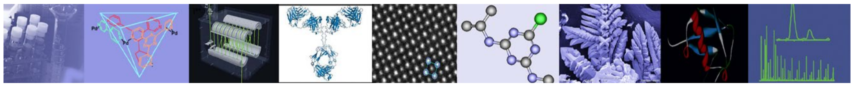
A small piece of commercial PA66 (Nylon 66) 0.28mg was measured without further sample preparation by using PY/GC/HRTOFMS, using the JMS-T200GC "*AccuTOF GCx-plus*" coupled with a PY-2020iD. Measurement conditions were shown in Table 1. To detect evolved gases by heating, we used a low filament current.

Table 1. Measurement Conditions

Instruments	JMS-T200GC *"AccuTOF GCx-plus"* (JEOL Ltd.)
	PY-2020iD (Frontier laboratories Ltd.)
Py conditions	
Furnace temp. program	60˚C -> 20˚C/min -> 700˚C (1min)
Py-GC-ITF temp.	350˚C
GC conditions	
Inlet temp.	350˚C
Inlet mode	Split 50 :1
Column	Blank tube (5 m x 0.25 mm)
Oven temp. program	350˚C (33 min)
Carrier gas flow rate	1 mL/min (He, Constant flow)
MS conditions	
Ionization method	EI(+) ; 25 V, 200 μA
GC-MS ITF temp.	350˚C
Ion source temp.	250˚C
Recording interval	2.5 Hz (0.4 sec/spectrum)
m/z range	10 ～ 800
Drift compensation	*m/z* 28.0056 ($N_2^{+\cdot}$)

Table 2 Assignment Results

Measured *m/z*	Chemical Formula	Calculated mass	Error ($\times 10^{-3}$ u)
18.0104	$H_2O^{+\cdot}$	18.0100	0.4
18.0344	NH_4^+	18.0338	0.6
27.9950	$CO^{+\cdot}$	27.9944	0.6
28.0180	CH_2N^+	28.0182	-0.2
28.0308	$C_2H_4^{+\cdot}$	28.0308	-0.0
43.9884	$CO_2^{+\cdot}$	43.9893	-0.9
44.0491	$C_2H_6N^+$	44.0495	-0.4



Results

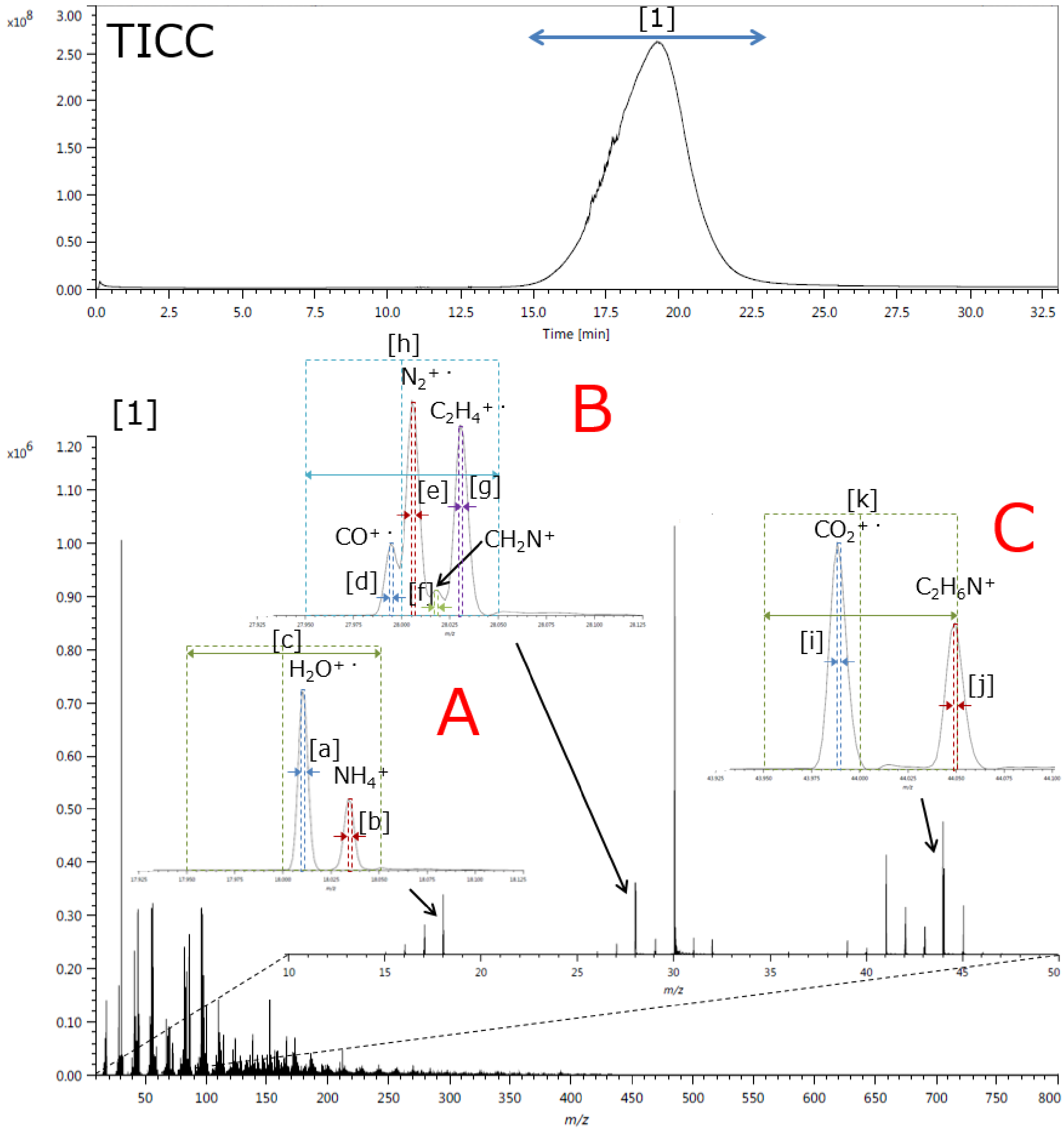


Figure 1. EGA thermogram and average mass spectrum

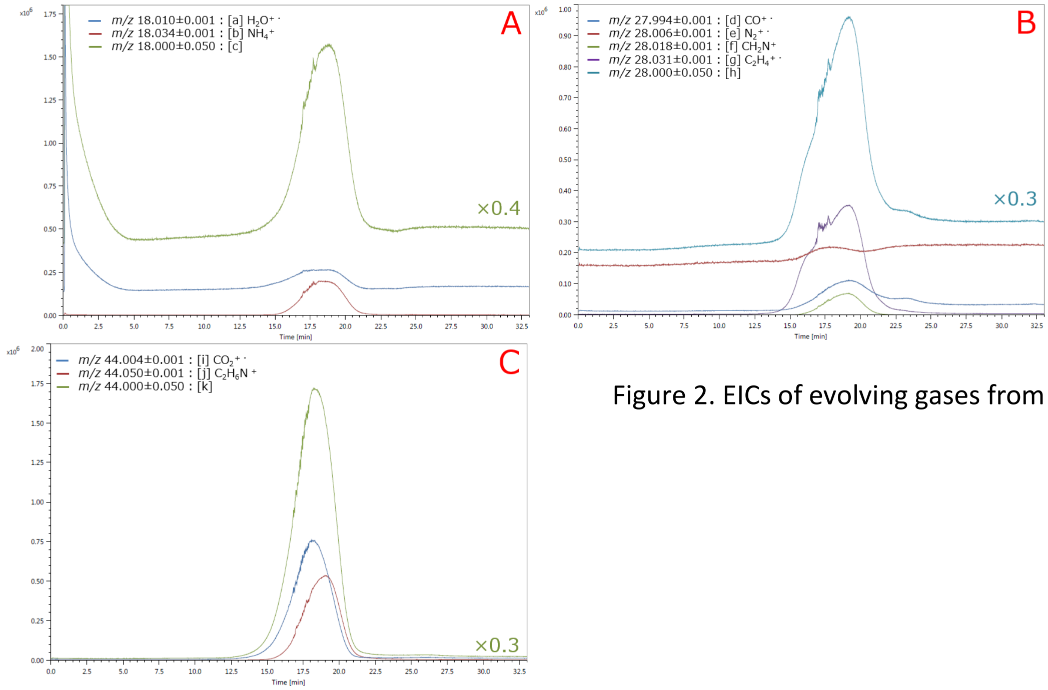


Figure 2. EICs of evolving gases from PA66

The average mass spectrum and the EGA thermogram are shown in Fig.1. In the average mass spectrum, two peaks were detected near *m/z* 18, four peaks were detected near *m/z* 28 and two peaks were detected near *m/z* 44 respectively. Table 2 shows the formulas for each compound. Figure 2 shows the extracted ion chromatogram (EIC) for the calculated *m/z* value ± 0.001 u. To compare the EIC created using exact *m/z* value with the EIC created using the nominal *m/z* value, figure 2 also shows the EIC created with nominal *m/z* value ± 0.050 u. The EIC of Fig. 2A shows no big difference from the behavior of each $H_2O^{+}\cdot$ (EIC [a]) and NH_4^{+} (EIC [b]). On the other hand, in the EIC of Fig. 2B shows slightly different behavior of each EIC [d], [e], [f], and [g]. The baseline intensity of EIC [e] includes contaminating N_2 in the He carrier gas cylinder and N_2 from a slight leak in the system. Although this level is originally high, generated N_2 due to thermal decomposition is shown near 410°C. In contrast, EIC [h] which assumes measurement with low-resolution MS looks like the integrated EICs of [d], [e], [f], and [g]. Likewise, EIC C in Fig. 2, the behavior of $CO_2^{+}\cdot$ (EIC [i]) and $C_2H_6N^{+}$ (EIC [j]) can be distinguished, and it was possible to clearly observe a slight difference in the behaviors of each compound.

Conclusion

A HRTOFMS can separate low molecular ions composed from carbon, hydrogen, nitrogen and oxygen. The Chemical formula of evolved gases can be determined with high accuracy. Py/GC/HRTOFMS results also permit monitoring the time- and temperature dependence of evolved gases with high accuracy from the measured exact masses. Consequently, PY/GC/HRTOFMS system is possible to monitor the behavior of low molecular weight compounds generated upon heating the polymer materials by high mass resolution.

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