Analysis of Polyethyleneimine using Field Desorption (FD) of JMS-T2000GC AccuTOF™ GC-Alpha

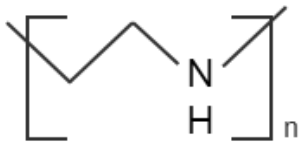
Product used: Mass Spectrometer (MS)

Introduction

Field Desorption (FD) is an ionization method that utilizes the tunneling effect in a high electric field generated between an emitter coated with a sample and an electrode to which a high voltage is applied. It is known as a soft ionization method that provides only molecular weight information because the internal energy given to the sample during ionization is low and fragmentation is unlikely to occur. In FD measurements, the sample-coated emitter is introduced directly to the ion source using a dedicated probe. Therefore, it is possible to measure difficult-to-volatile compounds, polar compounds, thermally unstable compounds, etc., which are difficult to measure with GC-MS. The combination of FD and time-of-flight mass spectrometer (TOFMS) enables calculation of the molecular formula of the measured compound. An overview of FD and sampling technique in the gas chromatograph time-of-flight mass spectrometer JMS-T2000GC AccuTOF™ GC-Alpha are described in MSTips No. 355 and MSTips No. 403.
In this MSTips, we report the analysis results of a water-soluble polymer polyethyleneimine (PEI), which contains many amines in its structure, by using FD of JMS-T2000GC.

Experimental

Commercially available polyethyleneimine (PEI) was used as the sample (Figure 1). PEI was prepared to 10 mg/mL using methanol. Then, 2 µL this sample was applied to the FI emitter for measurement. A gas chromatograph time-of-flight mass spectrometer JMS-T2000GC AccuTOF™ GC-Alpha was used for the measurements. An EI/FI/FD combination ion source was used, and FD was used as ionization method. Other detailed measurement conditions are shown in Table 1. Polymer analysis software “msRepeatFinder” was used for Kendrick Mass Defect (KMD) analysis.



Formula: $(C_2H_5N)_n$

Figure 1 Structural formula of PEI

Table 1 Measurement conditions

MS conditions	
Spectrometer	JMS-T2000GC AccuTOF™ GC-Alpha (JEOL Ltd.)
Ion Source	EI/FI/FD combination ion source
Ionization	FD+ (Cathode Voltage: -10kV, Emitter Current: 0 mA → 51.2 mA/min →50 mA)
Mass Range	*m/z* 50 – 3,200

Results

Figure 2 shows the TICC for this measurement. One peak derived from PEI was detected. Figure 3 shows the mass spectrum created at the location indicated by the blue arrow on the TICC. In the mass spectrum, some group of peaks with an interval of 43 u was observed. From the accurate mass measured, this was estimated to be the C_2H_5N of the monomer unit of PEI.

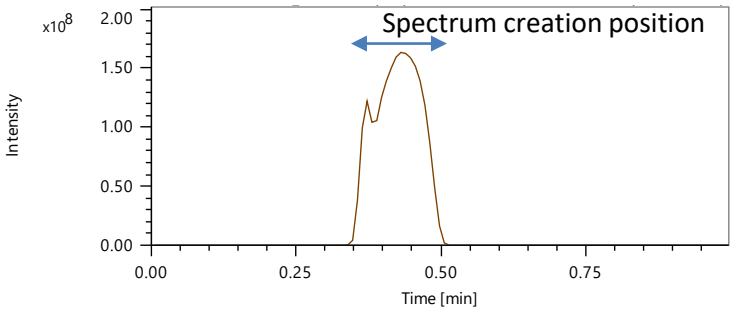


Figure 2 Total ion current chromatogram

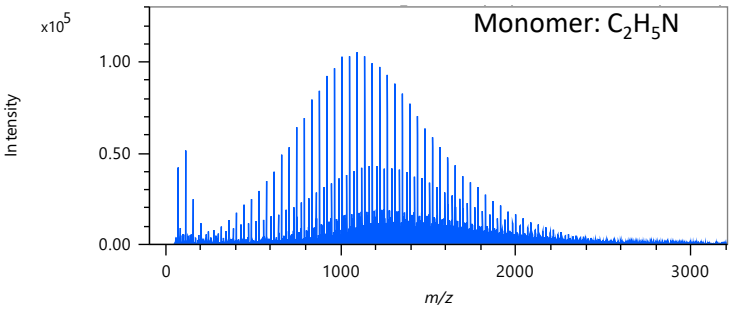


Figure 3 Mass spectrum of PEI

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Figure 4 is an expansion of the mass spectrum into a KMD plot using msRepeatFinder (base unit: C_2H_5N). The KMD plot confirmed four series (series A, B, C and D) with different end groups. Table 2 shows the structure estimation result of the end groups of series A (blue) and series B (red), which are major series that are strongly detected in mass spectrum. The most strongly observed series A was suggested to have end groups of H and NH_2, respectively. It was also suggested that series B has cyclic structure. Figure 5 shows the elemental composition estimated result for 20mer (*m/z* 878.87853) in series A. From this result, it was found that protonated polyethyleneimine ions were detected. The mass error was estimated to be 0.72 mDa, which was a good value. Furthermore, the elemental composition of series C was estimated two hydrogen atoms less than the composition of series B, and series D was estimated four hydrogen atoms less. These series are considered to be series B structures containing one or two additional cyclic structures or terminal double bonds.

These results indicate that even for polyethyleneimine, a water-soluble polymer containing a large amount of amines, ions with molecular weight information such as $[M+H]^+$ can be observed by FD , and the compositional formula can also be easily calculated.

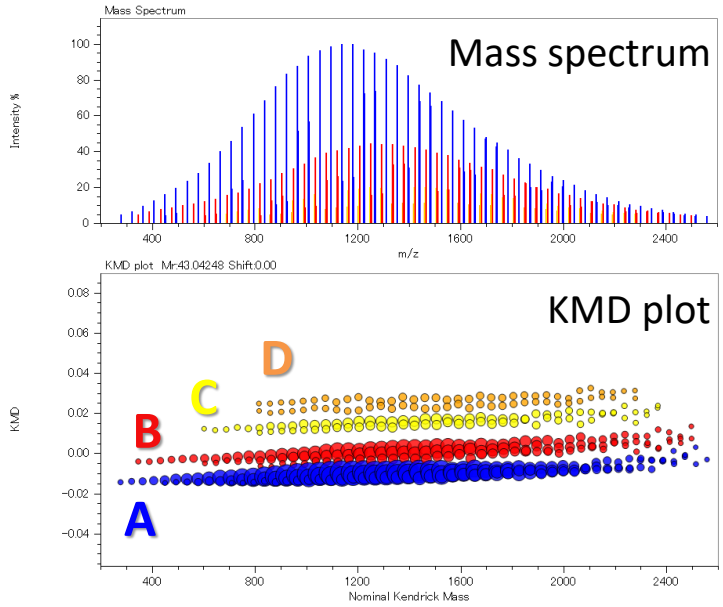


Table 2 Estimated structures result of end groups

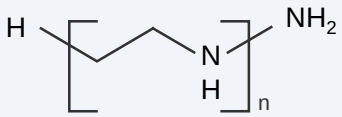
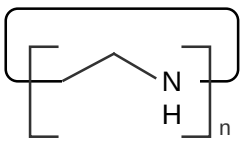
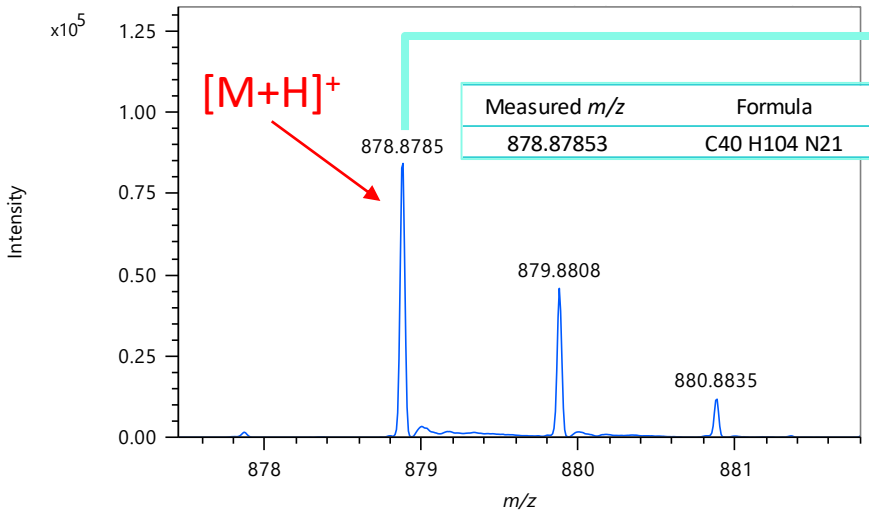
Series	Estimated structures
A	
B	

Figure 4 Mass spectrum and KMD plot



Measured *m/z*	Formula	Calculated *m/z*	Mass Error [mDa]
878.87853	C40 H104 N21	878.87781	0.72

Figure 5 Elemental composition estimated result of 20mer in series A

Conclusions

In this MSTips, we reported the analysis results of a water-soluble polymer PEI, which contains many amines in its structure, by using FD of JMS-T2000GC. As a result of the analysis, it was confirmed that protonated molecule related to molecular weight could be observed, and accurate mass could be obtained with good accuracy. Furthermore, the KMD plots in msRepeatFinder allowed us to easily visualize the series with different end groups. These results indicate that FD is useful for the analysis of polymeric materials.

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