# Structure Analysis of Polyphenylene Sulfide End Groups using Field Desorption (FD) of JMS-T2000GC AccuTOF™ GC-Alpha

Product used: Mass Spectrometer (MS)

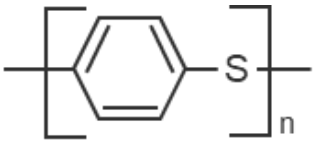
## Introduction

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. The combination of FD and time-of-flight mass spectrometer (TOFMS) enables calculation of the molecular formula of the measured compound. The 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 measurement result of Polyphenylene Sulfide (PPS), an engineering plastic with excellent heat and chemical resistance. It is known that differences in the manufacturing process of PPS appear in the end groups, so structure analysis of the end groups is important. However, PPS is difficult to measure by LC-MS because it is insoluble in common solvents. Therefore, the end groups were estimated using FD, which can measure PPS oligomers even when they are dispersed in a solvent.

## Experimental

We used a research grade PPS (Scientific Polymer Products, Figure 1) as a test sample in this experiment. PPS was prepared to 10 mg/mL in THF. 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 measurement. 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: $(C_6H_4S)_n$

**Figure 1 Structural formula of PPS**

**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 PPS 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 108 u was observed. From the accurate mass measured, this was estimated to be the $C_6H_4S$ of the monomer unit of PPS.

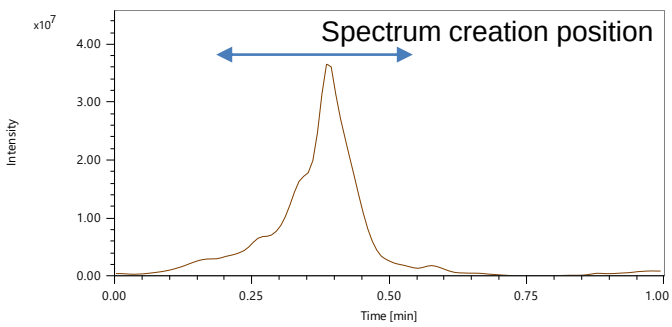



**Figure 2 Total ion current chromatogram**

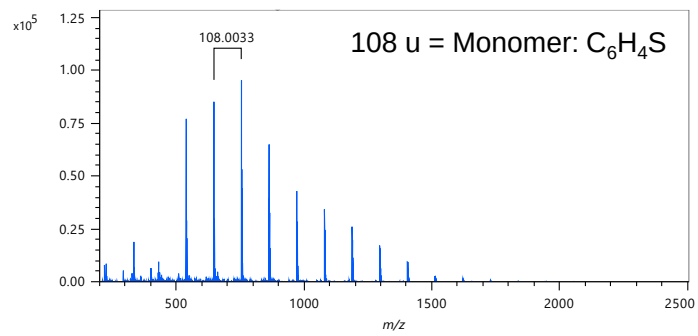



**Figure 3 Mass spectrum of PPS**



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Figure 4 is an expansion of the mass spectrum into a KMD plot using msRepeatFinder (base unit: $C_6H_4S$). The KMD plot confirmed three series (series A, B, and C) with different end groups. Table 2 shows the results of structural estimation of the end groups for each series based on accurate mass analysis and isotopic patterns. The highest intensity series A had a cyclic structure. Series B was suggested to have a structure containing chlorine. Since isotopic patterns such as M+2 become characteristic when chlorine is included, we compared the simulated results of isotopic patterns with the measured spectrum. Figure 5 shows the elemental composition estimated result and molecular ion isotope pattern simulation result for the tetramer (*m/z* 577.97969) of series B. The mass error was calculated to be -2.26mDa, and the accurate mass was obtained with good accuracy. Furthermore, the isotope pattern was generally similar to the simulation result.

PPS is industrially produced mainly by the Phillips process[1]. The Phillips process is a method in which dichlorobenzene and sodium sulfide are reacted in N-Methyl-2-Pyrrolidone.It has been reported that PPS synthesized by this process contains a component with a chlorophenyl group at the end[1]. In this result, since series B contains a chlorophenyl group at the end, this sample was presumed to have been manufactured by the Phillips process.

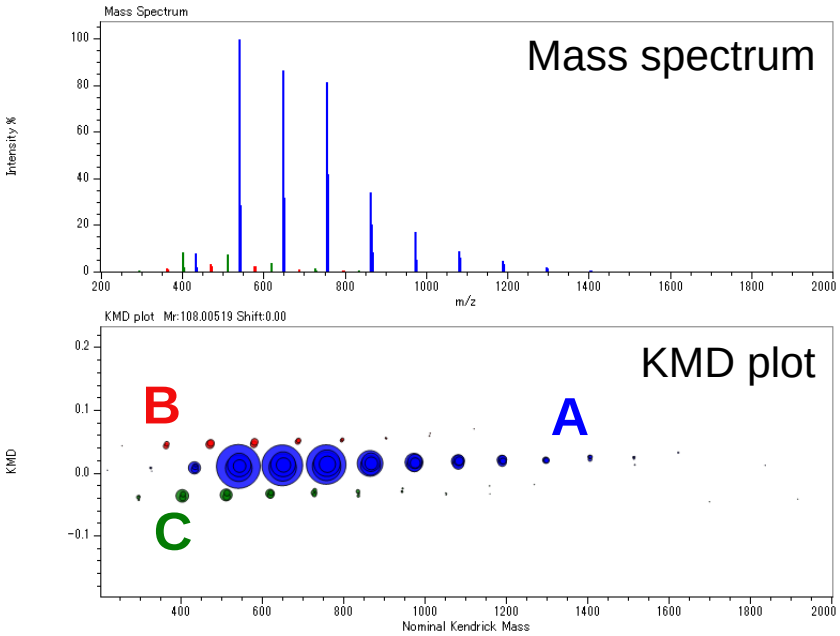



**Table 2 Estimated structures result of end groups**

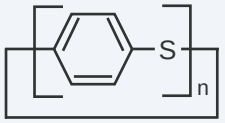
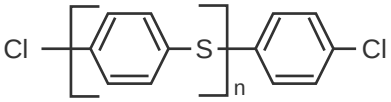
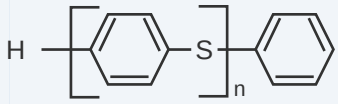
| Series | Estimated structures |
|---|---|
| A |  |
| B |  |
| C |  |

**Figure 4 Mass spectrum and KMD plot**

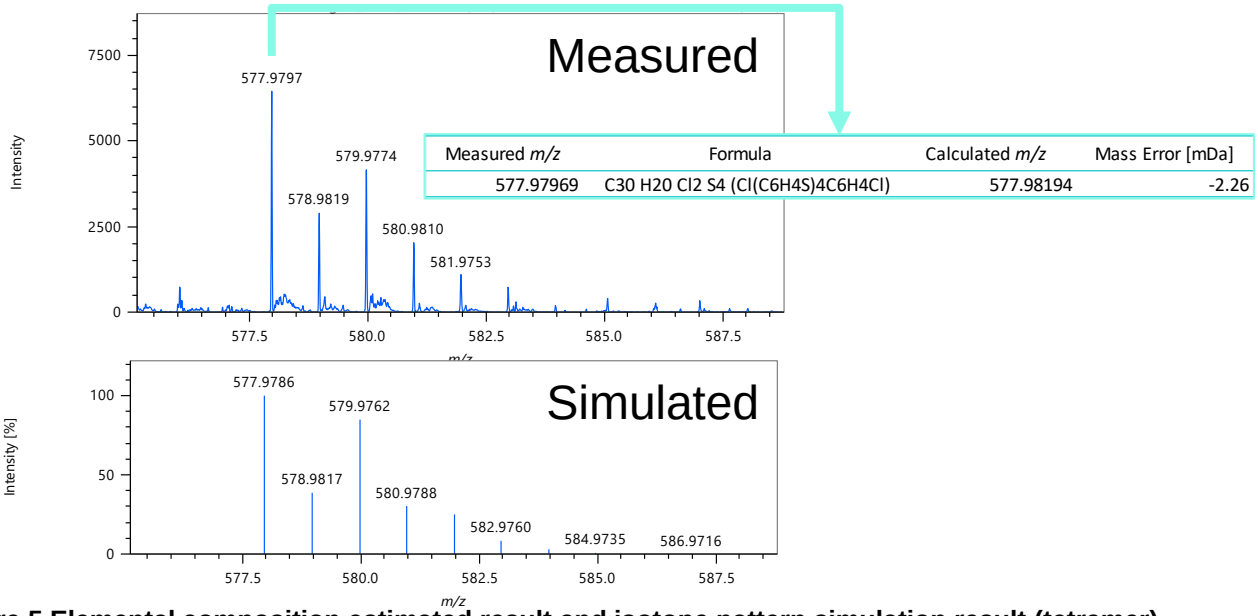



**Figure 5 Elemental composition estimated result and isotope pattern simulation result (tetramer)**

## Conclusions

In this MSTips, we reported the estimation results of PPS end groups using FD. By using FD, we were able to analyze PPS, which is difficult to measure with LC-MS because it is insoluble in common solvents. Furthermore, the KMD plots in msRepeatFinder allowed us to easily visualize the series with different end groups and ultimately estimate the manufacturing process. These results indicate that FD is useful for the analysis of polymeric materials.

## Reference

1) Sayaka Nakamura, et al. BUNSEKI KAGAKU Vol. 70, No1・2, pp. 45-51 (2021)



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