End group structural analysis of polyphenylene sulfide by Direct Insertion Probe(DIP)-MS/MS

Product used : Mass spectrometer(MS)

Introduction

Pyrolysis/gas chromatography/mass spectrometry (Py/GC/MS) and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) are powerful tools in polymer analysis. In addition to these methods, end group analysis of polymer by thermal desorption / pyrolysis (TDP) - DART-MS has been proposed recently[1, 2]. This is a method of analyzing the volatile components generated when the polymer is gradually heated by a thermal desorption / pyrolysis device by using DART-MS. By gradual heating, unlike Py/GC/MS, moderately fragmented oligomer components can be analyzed by DART-MS. Some of the oligomer components generated include the end group structure by single cleavage of the main chain, which helps to analyze the structure of the polymer. We have already reported an example of analysis of polyphenylene sulfide (PPS) by TDP-DART-MS in MSTips No. 353[3]. In this application, the same PPS was used as measurement sample, and DIP was used as a heating device. We report on the observation of four series of PPS with different end groups reported in MSTips No. 353 by DIP-MS and the structural analysis of the end groups by DIP-MS/MS.

Method

The measurement was performed using DIP and GC triple quadrupole mass spectrometer JMS-TQ4000GC UltraQuad™ TQ. PPS(Scientific Polymer Products, Inc.) for research was used as the measurement sample. The DIP analysis was performed under the measurement condition shown in Table 1.

Table 1 Measurement condition

DIP condition	
Heating Program	80 ℃ (0.1 min) → 256 ℃/min → 500 ℃ (6.0 min)
MS condition	
Ion Source Temp.	250 ℃
Ionization Mode	EI+, 70 eV
Measurement Mode	SCAN, Product Ion SCAN
Collision Gas	N_2, 10%

Result

- Analysis of end group series by DIP-MS

The obtained TICC by DIP-MS is shown in Fig. 1(a). The mass spectrum at RT 0.5-2.4 min (Temp. around 200-500 ℃) is shown in Fig. 1(b). The lower molecular weight region less than *m/z* 500 is prominently detected at this RT. Four series of PPS with different end groups reported in MSTips No. 353 were observed. It can be confirmed that the repeating unit is observed at 108 u of C6H4S. PPS containing chlorine atoms in the end group can also be confirmed presence of chlorine atoms from the characteristic isotope pattern in the EI mass spectrum.

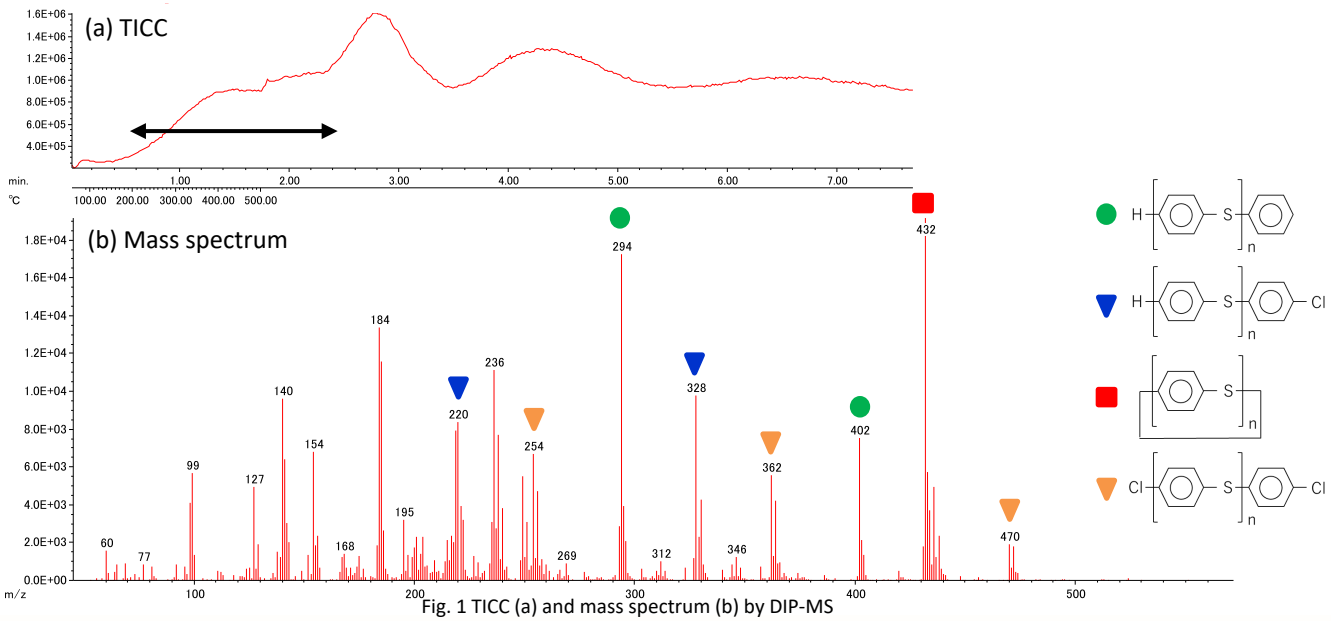

Fig. 1 TICC (a) and mass spectrum (b) by DIP-MS

JEOL Ltd.
3-1-2 Musashino Akishima Tokyo 196-8558 Japan Sales Division Tel. +81-3-6262-3560 Fax. +81-3-6262-3577
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● Measurement results by DIP-MS/MS

Structural analysis of the ● and ▼ series of high peak intensity observed by DIP-MS was performed from product ion scan measurement. The product ion spectra are shown in Fig. 2. In common, cleavage at the thioether bond was characteristic observed. On the other hand, when the end group contain a chlorine atom, cleavage from the chlorine atom was also observed characteristically. *m/z* 219 in Fig. 2 (b) is a cleavage at the thioether bond, which is estimated to be cleavage to the end group containing a chlorine atom, but the presence or absence of chlorine atom cannot be determined from the isotopic pattern because there are not isotope peaks in the product ion scan measurement. In addition, since the obtained m/z value is nominal mass, it is not possible to confirm the elemental composition by accurate mass. Therefore, we selected *m/z* 330 as the precursor ion, which is estimated to contain ^{37}Cl with a 2 u difference from the precursor ion at *m/z* 328. The product ion spectrum at *m/z* 330 is shown in Fig. 2 (c). Only the peak at *m/z* 219 was observed as *m/z* 221 with a 2 u shift. Thus, *m/z* 219 was confirmed to be a cleavage to the end group including a chlorine atom. On the contrary, m/z 293 and m/z 185 are not shifted, confirming that the cleavage is to the end group without chlorine atom.

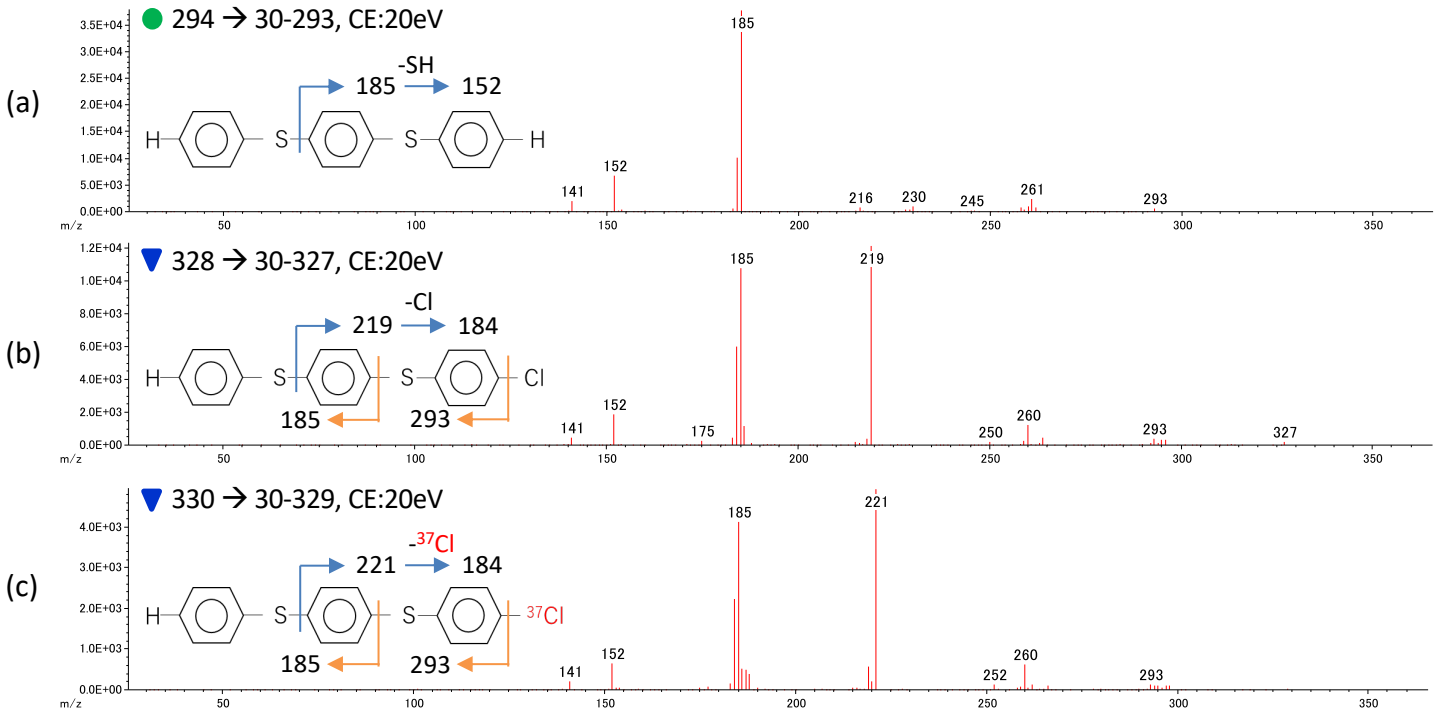

Fig. 2 Product ion spectra at *m/z* 294 (a), *m/z* 328 (b) and *m/z* 330 (c)

Conclusion

For DIP-MS, it was possible to obtain the same information as polymer analysis by TDP-DART-MS. For DIP-MS/MS, It was possible to perform structural analysis of the end group. Especially, when a characteristic atom such as chlorine is included, it is possible to confirm which side of the end group is involved in the cleavage by selecting a different stable isotope m/z value as the precursor ion and comparing the obtained product ion spectra. Thus, the JMS-TQ4000GC UltraQuad™ TQ was shown to be an effective analytical instrument for the structural analysis of polymer end group.

References

[1] Sato Hiroaki, et al., BUNSEKI KAGAKU Vol. 69, No1・2, pp. 77-83 (2020)
[2] Sayaka Nakamura, et al. BUNSEKI KAGAKU Vol. 70, No1・2, pp. 45-51 (2021)
[3] MSTips No. 353

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