

Analysis of low molecular weight polyethylene with solvent-free method using JMS-S3000 "SpiralTOF™"

Product used : Mass spectrometer (MS)

Matrix assisted laser desorption ionization (MALDI) time-flight mass spectrometer (TOFMS) is a powerful tool to identify the repeat units and end groups of polymers. The mass spectra of polymers can be easily interpreted because MALDI can generate singly-charged ions over a wide mass range. MALDI is a soft ionization method that uses "matrix" compounds and "cationization agents" to assist the ionization process of polymers. Typically, sample, matrix and cationization agent are dissolved in the same solvent. These solutions are pre-mixed and placed drop-wise on the target plate to make cocrystals (dried droplet method). However, this procedure cannot be applied to polymers that are insoluble or only slightly soluble. To solve this problem, solvent-free methods have been developed [1-4] for these situations. In this report, we analyzed low molecular weight polyethylene by using a solvent-free method and then using a high mass-resolution MALDI-TOFMS "SpiralTOF™" system for the analysis.

Experiments

Sample : Polyethylene analytical standard, for GPC, 1,000
(Sigma aldrich PN 81219) (PE1000)

Matrix: trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile
(DCTB)

Cationization Agent: Silver Trifluoroacetate (AgTFA)

Preparation: PE1000, DCTB, and AgTFA powders were mixed in Agate mortar. The mixed powder was then pressed onto the target plate using a spatula (Note 1).
(See Figure 1)

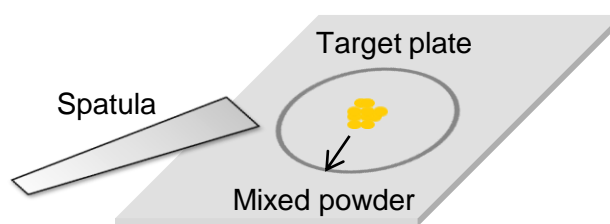


Figure 1 Solvent-free sample preparation.

Measurement: The mass spectra were acquired by using SpiralTOF™ positive ion mode.

Results

The PE1000 mass spectrum is shown in Figure 2. The polymer distribution of $[H(C_2H_4)_nH + Ag]^+$ was observed from 600 – 1,800 where the apex is at m/z 1000 (Figure 2a). The enlarged mass spectrum at m/z 890 - 960, where $[H(C_2H_4)_nH + Ag]^+$ ($n = 28 - 30$) were observed, is shown in Figure 2b. The peaks had a mass resolution of more than 50,000, and the mass difference $28.031 \text{ u} \pm 0.001 \text{ u}$ corresponded with mass of polyethylene repeat unit C_2H_4 . In the solvent-free method used in this report, the mixed powder of sample, matrix, and cationization agent were pressed onto the target plate. The sample surface roughness is much larger than for the dried droplet method. Even so, the SpiralTOF™ was able to achieve high mass-resolution and mass accuracy using the system's 17m flight path in order to overcome the adverse effects of sample roughness.

References

- [1] R. Sketton, F. Doubois, K. Zenobi, *Anal. Chem.* 72 (7) (2000) 1707–1710
- [2] L. Przybilla, J. D. Brand, K. Yoshimura, H.J. Räder, K. Müllen, *Anal. Chem.* 72 (2000) 4591–4597
- [3] A. Marie, F. Fournier, J.C. Tabet, *Anal. Chem.* 72 (2000) 5106–5114
- [4] S. Trimpin, A. Rouhanipour, R. Az, H.J. Räder, K. Müllen, *Rapid Commun. Mass Spectrom.* 15 (2001) 1364–1373

(Note 1) Please press the powder firmly onto the plate in order to prevent ion source contamination from the scattering of powders.

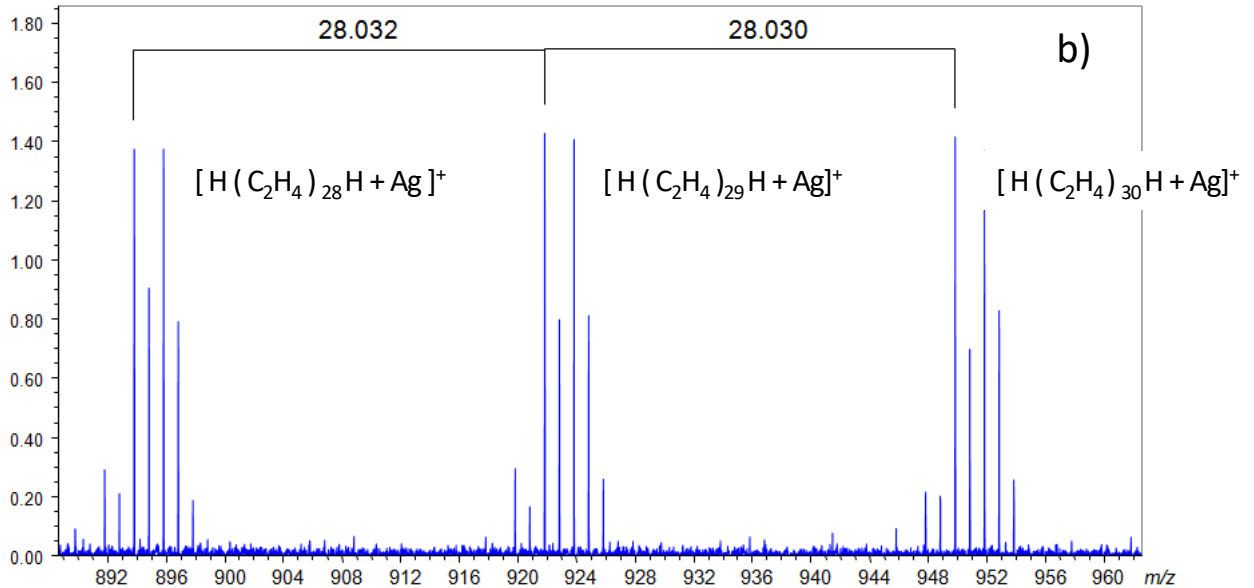
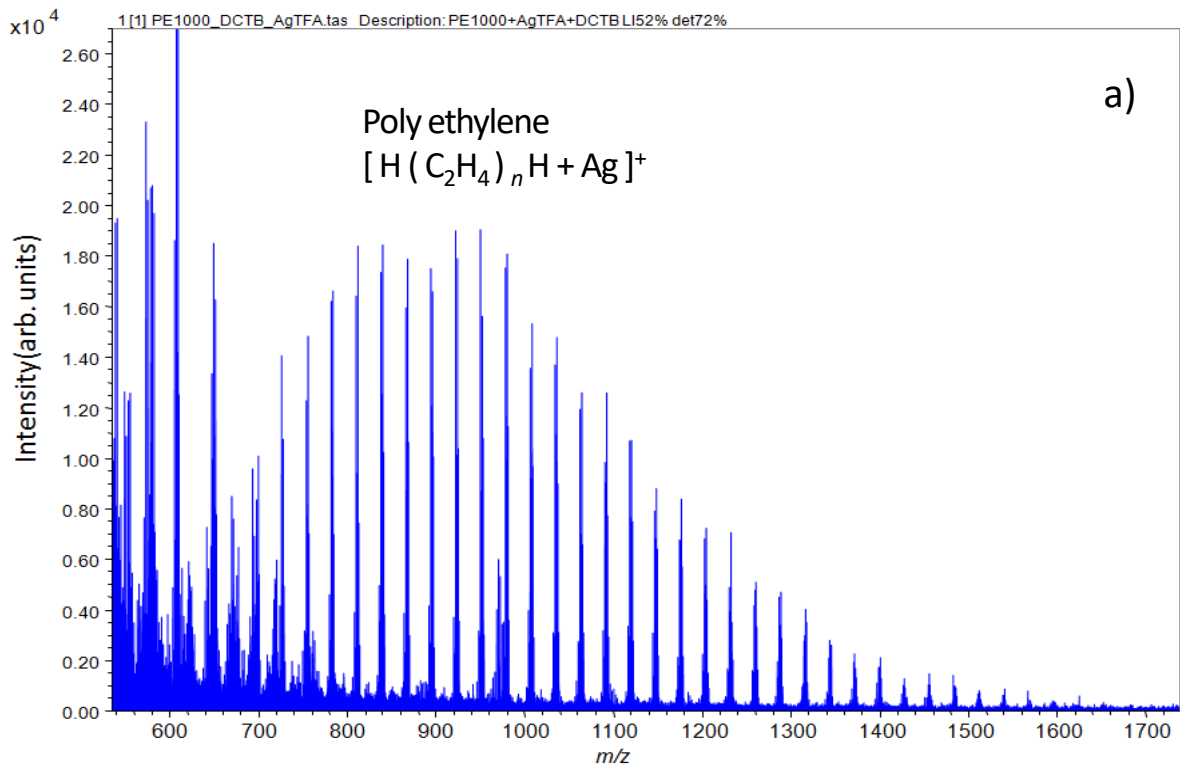


Figure 2 a) Mass spectrum of PE1000. b) Distribution of $[H(C_2H_4)_nH + Ag]^+$ was observed around m/z 1000.

