AccuTOF-GCv Series

Analysis of Polydimethylsiloxanes

Introduction

Three polydimethylsiloxane compounds: octamethylcyclotetrasiloxane (sample 1), decamethylcyclopentasiloxane (sample 2) and octa(dimethylsiloxy)silsesquioxane (sample 3), were analyzed using a GC/TOFMS. The first two samples are relatively small molecules with molecular weights of 296 and 370, respectively, so they were introduced into the system through the mass reference sample inlet (reservoir). Sample 3 is a much bigger molecule with a molecular weight of 1,016 that could not be introduced through the reservoir. As a result, this sample was introduced by injecting it into the GC.

For this work, each sample was analyzed by using the JEOL AccuTOF-GC with both EI (hard ionization) and FI (soft ionization).

Methods

Samples

1.Octamethylcyclotetrasiloxane,$C_8H_{24}O_4Si_4$, Neat
2.Decamethylcyclopentasiloxane, $C_{10}H_{30}O_5Si_5$, Neat
3.Octa(dimethylsiloxy)silsesquioxane, $C_{16}H_{56}O_{20}Si_{16}$, 2 mg/ml in acetone

GC conditions

Column: ZB-5ms, 30 m x 0.25 mm, 0.25 µm
Injector: 320 °C, 1 mL/min (constant flow mode,) split mode (50:1)
Oven: 50 °C (1 min) → 20 °C/min → 320 °C (5.5 min)

MS conditions

Mass spectrometer: JMS-T100GC "AccuTOF GC"
EI ionization: Electron energy: 70 eV
Ionization current: 300 µA
FI ionization: Cathode potential: -10 kV
Emitter current: 7 mA for 20 msec between spectra
Temperatures: Ion source: 280 °C
GC-ITF: 280 °C
Reservoir: 100 °C
Acquired mass range: *m/z* 35 – 1,400
Spectral recording interval: 0.4 sec

Results and Discussion

The acquired electron ionization (EI) mass spectra for samples 1 and 2 are shown in Fig. 2. For both compounds, the base peaks were the $[M\text{-}CH_3]^+$ ions and no molecular ion peaks were detected in this ionization mode. The major peaks, as documented in Table 1, offer a good possibility for use as internal mass references for accurate mass measurements. When these compounds were analyzed by field ionization (FI), the base peaks were still the $[M\text{-}CH_3]^+$ ions with virtually no molecular ions or fragment ions detected (data not shown).

The EI and FI mass spectra for octa(dimethylsiloxy)silsesquioxane are shown in Fig. 3. Characteristic ions such as $[M\text{-}CH_3]^+$ at *m/z* 1000.94 and $[M\text{-}H]^+$ at *m/z* 1014.96 were observed in both mass spectra. In the EI spectrum, there were also several fragment ions that were common to both samples 1 and 2, including the *m/z* 73.05. However, in the FI spectrum, the only ions observed were the *m/z* 1000.94 and *m/z* 1014.96 mentioned previously.

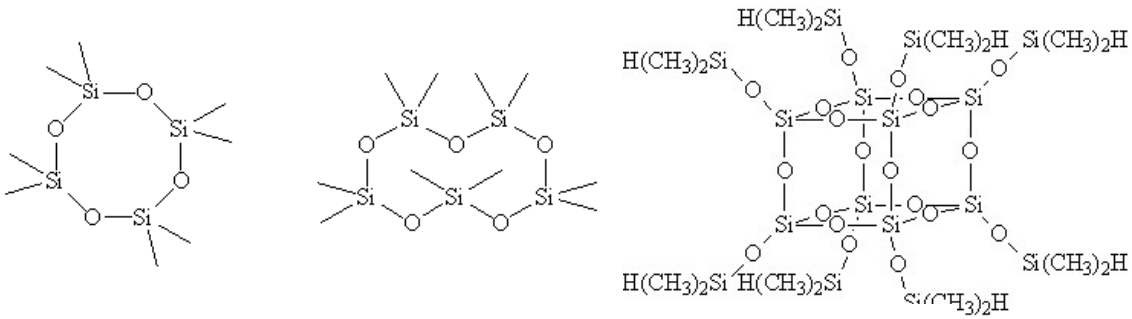

Fig. 1 Structural formulae of the samples

Conclusions

Each polydimethylsiloxane sample generated a strong $[M\text{-}CH_3]^+$ ion for both EI and FI. However, the molecular ions for these samples were difficult to detect, even when using the soft ionization FI technique. Additionally, samples 1 and 2 offer good possibilities as internal standards for accurate mass measurements.

Acknowledgement

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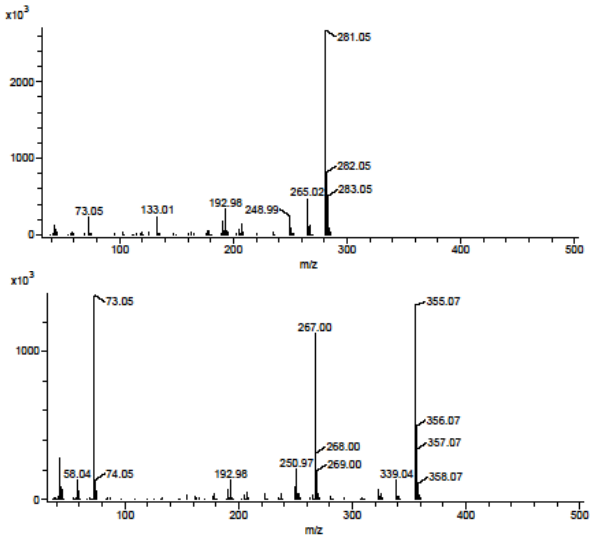

Fig.2 Mass spectra of Octamethylcyclotetrasiloxane (upper) and Decamethylcyclopentasiloxane (lower) by EI.

	Calculated exact mass	Fomula
Octamethylcyclo tetrasiloxane	73.04735	C_3H_9Si
	248.98909	$C_5H_{13}O_4Si_4$
	265.02039	$C_6H_{17}O_4Si_4$
	281.05169	$C_7H_{21}O_4Si_4$
Decamethylcyclo pentasiloxane	73.04735	C_3H_9Si
	266.99965	$C_5H_{15}O_5Si_4$
	355.07048	$C_9H_{27}O_5Si_5$
Octa(dimethylsiloxy) silsesquioxane	1000.94384	$C_{15}H_{53}O_{20}Si_{16}$
	1014.95949	$C_{16}H_{55}O_{20}Si_{16}$

Table1. Calculated exact mass for each ion.

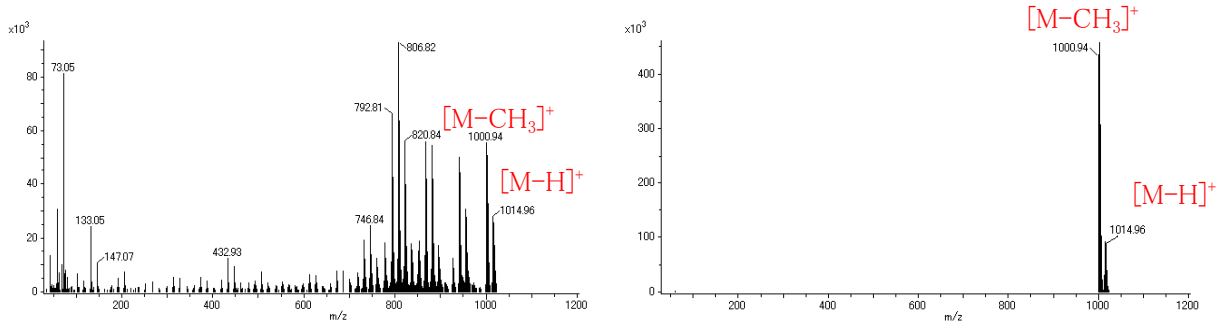

Fig.3 Mass spectrum of Octa(dimethylsiloxysilsesquioxane by EI (left) and FI (right).