Effect of hydrogen carrier gas on Py-GC/MS analysis of polymers
Part 2 Hydrogenation of HDPE pyrolyzates in EI source of MS

[Background] The previous Technical Note (PYA4-007E) revealed that the pyrolysis (Py)-GC/MS of high density polyethylene (HDPE) in a hydrogen (H_2) atmosphere altered the peak intensity ratios of diolefin (C_n"), monoolefin (C_n') and alkane (C_n) from those obtained in a helium (He) atmosphere. The difference is attributed to the hydrogenation of unsaturated bonds formed during the pyrolysis process. This note examines the differences in the HDPE pyrolyzates formed when the pyrolysis is performed in either a He or a H_2 atmosphere.

[Experimental] 200 µg of HDPE powder was placed in a deactivated stainless steel sample cup (i.d.=4 mm, *H*=8 mm) and pyrolyzed at 600ºC. The analytical system used for the Py-GC/MS analysis consisted of a Multi-Shot Pyrolyzer (EGA/PY-3030D) with an Auto-Shot Sampler (AS-1020E) interfaced directly to the split injector of a GC/MS system. An Ultra ALLOY® metal capillary column (UA$^+$-5) was used as a separation column. The flow rate of He or H_2 carrier gas was 1 mL/min.

[Results] Pyrograms of C_{14} region of HDPE pyrolyzates along with MS spectra of C_{14}' are shown in Fig. 1. Note that because H_2 has a larger linear velocity in the column, the retention times for C_{14} peaks in H_2 atmosphere are smaller than those in He. When the pyrolysis is done in a He atmosphere the peak intensity for the $[M+2]^+$ (*m/z* 198) ion is extremely low. While, when the pyrolysis is done in a H_2 atmosphere, the $[M+2]^+$ peek is easily identified. This may be because the unsaturated bonds present in the pyrolyzates are partly hydrogenated during the separation process or on the surface of the MS ion source itself. Consequently, the peak intensity ratios observed in the two gases are significantly different. This work clearly illustrates that when H_2 is used as a carrier gas, the hydrogenation of unsaturated pyrolyzates may occur.[1)]

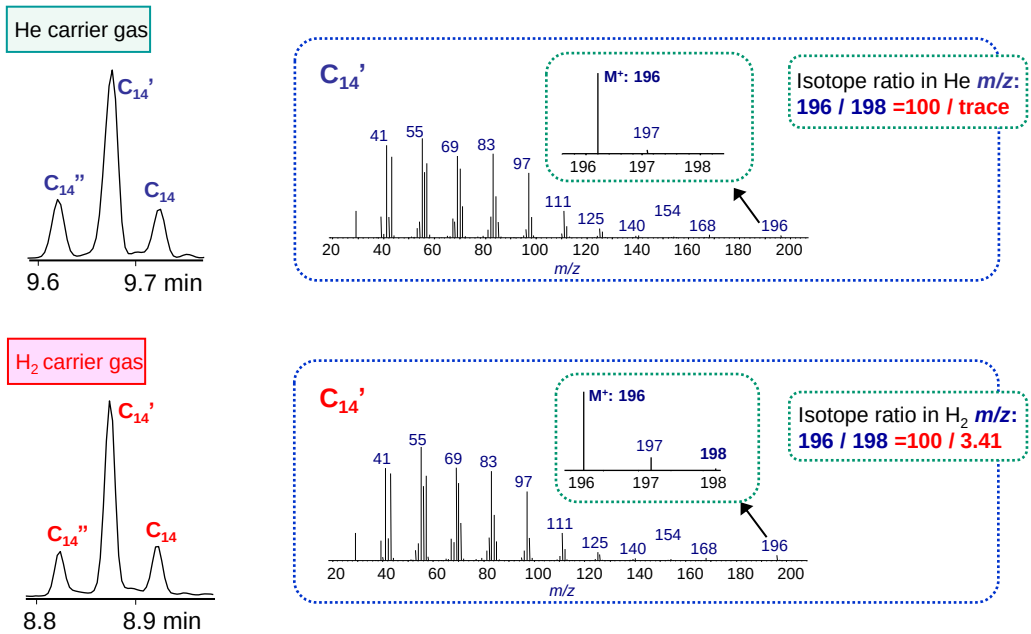

Fig. 1 Pyrograms of C_{14} region of HDPE pyrolyzates and MS spectra of C_{14}'

Pyrolysis Temp.: 600ºC, GC oven temp.: 40 (2 min) – 320 ºC (20 ºC/min, 3 min hold)
Separation column: UA$^+$-5 (5% diphenyl 95% dimethylpolysiloxane), *L*=30 m, i.d.=0.25 mm, df=0.25 µm
Column flow rate: 1 mL/min, Split ratio: 1/100, Sample: HDPE (200 µg)

[1)] Reproduced from A. Watanabe, *et al.*, *Anal. Chem.*, 88 (2016) 5462–5468

Keywords : H_2 carrier gas, saturated/unsaturated hydrocarbons, hydrogenation, Py-GC/MS, HDPE, MS ion source, isotope ratio

Products used : Multi-functional pyrolyzer, Auto-Shot Sampler, UA$^+$-5

Applications : General polymer analysis

Related technical notes : PYA4-007E, PYA4-009E

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