Effect of hydrogen carrier gas on Py-GC/MS analysis of polymers

Part 1 Hydrogenation of HDPE pyrolyzates

[Background] When pyrolysis is done in hydrogen (H_2), there is a possibility that hydrogenation of pyrolyzates may occur during the pyrolysis and/or ionization steps, which will yield a mass spectrum that is different from that obtained in a helium (He) atmosphere. If the differences are large, the library search may be rendered useless, since the libraries were constructed based on mass spectra obtained in a He atmosphere. This note (Part 1) describes the impact of the H_2 carrier gas on the mass spectra, when high density polyethylene (HDPE) is pyrolyzed in the presence of metal residues.

[Experimental] HDPE was freeze-pulverized and 100 µg of the powder was placed in a deactivated stainless steel sample cup. The Py-GC/MS system consisted of a Multi-Shot Pyrolyzer (EGA/PY-3030D) was directly interfaced to the injection port of a GC/MS. The separation column used was a metal capillary column (Ultra ALLOY⁺-5). He or H_2 was used as a carrier gas and the flow rate was 1 mL/min. The sample was pyrolyzed at 600ºC and the pyrolyzates were analyzed by GC/MS.

[Results] Pyrograms obtained in He and H_2 atmospheres (Fig. 1) reveal the differences in the peak height between diolefin (C_n") and alkane (C_n). For example, the peak area of diolefin (C_{14}") is larger than that of alkane (C_{14}) for He carrier gas. Whereas, the ratio is reversed (Fig. 1) for H_2 carrier gas. This difference can be attributed to the hydrogenation of C_{14}" to mono-olefin (C_{14}') and C_{14}' to C_{14} (Fig. 2.). In contrast to HDPE, low density polyethylene (LDPE) did not show hydrogenation during Py-GC/MS experiments under H_2 atmosphere. Accordingly, the hydrogenation reaction can be ascribed to the metal residues in HDPE, because LDPE is manufactured without metal catalysts as listed in Table 1. Since the hydrogenation of HDPE occurs only to a limited degree, library search results are unaffected by changing the carrier gas from He to H_2.

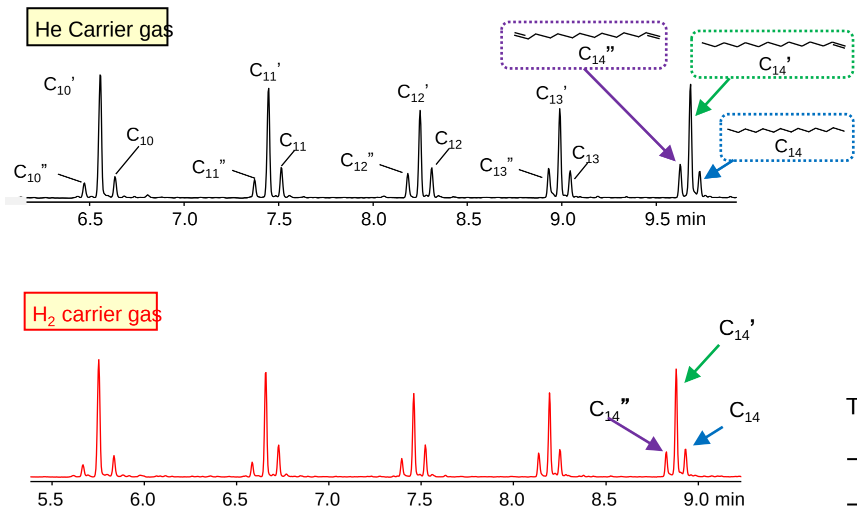

Fig. 1 Pyrogram of HDPE in He and H_2 atmosphere

Pyrolysis Temp.: 600ºC, GC oven Temp.: 40 (2 min) - 320ºC (20 ºC/min, 3 min hold)
Separation column: Ultra ALLOY⁺-5 (5% diphenyl 95% dimethylpolysiloxane),
L=30 m, i.d.=0.25 mm, d.f.=0.25 µm
Column flow rate: 1 mL/min, Split ratio: 1/100, Sample: HDPE (0.1 mg)

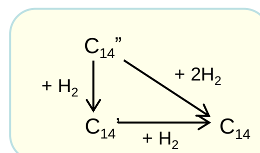

Fig. 2 Formation of alkane by hydrogenation of di- and mono olefins

Table 1. Residual metals in HDPE and LDPE (ppm, XRF analysis)[1)]

Polymer	Mg	Ti	Cr	Zr	Al
HDPE	10	11	3	2	38
LDPE	0	0	0	0	0

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

Keywords : H_2 carrier gas, Hydrogenation, Py-GC/MS, High density polyethylene, HDPE, Saturated and unsaturated hydrocarbons

Products used : Multi-functional pyrolyzer, UA⁺-5

Applications : General polymer analysis

Related technical notes : PYA4-008E, PYA4-009E

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