Pyrolysis–Hydrogenation Glass Capillary Gas Chromatographic Characterization of Polyethylenes and Ethylene–α-Olefin Copolymers

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ABSTRACT: Characteristic high-resolution pyrograms of polyolefins such as various polyethylenes (PE) and ethylene–α-olefin copolymers were obtained using an improved pyrolysis–hydrogenation glass capillary gas chromatography. By simple comparison of the corresponding pyrograms, it is possible to qualify the nature and the relative amount of the short branches such as methyl, ethyl, and butyl in low-density PE and the minor comonomer components in ethylene–α-olefin copolymers.

It has been recognized that the morphology and many physical properties of polyethylenes (PE) are keenly dependent upon the nature and the amount of both short and long branches along the polymer backbone. Most of the studies on characterization of the chain branching were done by IR,[1-4] ^{1}H NMR,[4-6] and ^{13}C NMR.[4,8,9] The pioneering work by Willbourn[1] utilized the IR method together with γ-ray radiolysis followed by identification of the gaseous hydrocarbons by mass spectrometry. On the other hand, pyrolysis–gas chromatography (pgc) was also demonstrated to be a simple but powerful technique for studying the chain branching of polyolefins.[10-15] Most of the pgc work made use of in-line hydrogenation followed by pyrolysis to simplify the resulting degradation products. The separation of the peaks appearing on the reported pyrograms, however, was still not sufficient for the complete assignment of the characteristic products which pertain to the branching structures.

The fact that so many attempts have been made on this problem, however, suggests that there still exist inconsistent arguments about the interpretation of the associated spectra and pyrograms, and that the characterization of the branching structures has room for further refinements.

In this work, high-resolution pyrograms of polyolefins such as high-density PE (HDPE), low-density PE (LDPE), and various model copolymers between ethylene and α-olefins were obtained by an improved pyrolysis–hydrogenation device directly attached to a high-resolution glass capillary gas chromatograph using a modified splitter system described in detail elsewhere.[16] It was demonstrated that the short branches in PE and the minor comonomer composition in ethylene–α-olefin copolymers can easily be interpreted in terms of the nature and the relative amount by simple comparison of the well-resolved characteristic peaks on the corresponding pyrograms.

Experimental Section

Samples. Four kinds of commercial PE were used: (a) LDPE-1 with density of 0.921 g/cm^3 and LDPE-2 with density of 0.919 both of which were synthesized by the high-pressure polymerization process, (b) HDPE with density of 0.958 by the medium-pressure process, and (c) HDPE with density of 0.963 by the low-pressure process. Three types of commercial ethylene–α-olefin copolymers were also studied as reference materials: (a) ethylene–propylene copolymer (P(E-*co*-P)) with density of 0.931 containing 6.3 wt % of propylene, (b) ethylene–1-butene copolymer (P(E-*co*-butene)) with density of 0.921 containing 10.1 wt % of 1-butene, and (c) ethylene–1-hexene copolymer (P(E-*co*-hexene)) with density of 0.938 containing 1.5 wt % of 1-hexene.

Apparatus. A vertical microfurnace-type pyrolyzer (Yanagimoto, GP-1018) described in detail elsewhere[16,17] was directly attached to a gas chromatograph (Shimadzu, 7AG) with a glass capillary column and FID (Figure 1). As shown in Figure 1, a precut column (B) (i.d., 3 mm × 5 cm long) containing Diasolid H (80–100 mesh) coated with 5 wt % of OV-101 and a hydrogenation catalyst column (C) (i.d., 3 mm × 30 cm long) containing Diasolid H (80–100 mesh) coated with 10 wt % of Pt were inserted in series between the pyrolyzer (A) and the splitter (D) for the capillary column. The former precut column was used to protect the catalyst and the highly efficient glass capillary column from tarry and/or involatile degradation products which otherwise result in a loss of the resolution. Both the catalyst and the precut columns were maintained at 200 °C. On the other hand, the splitter was independently held at the maximum temperature of the separation column, 250 °C, to attain quantitative and reproducible splitting for the complex mixtures of the degradation products with a wide range of volatility.[16]

Pyrolysis–Gas Chromatographic Conditions. A glass capillary column (o.d. 0.9 mm × i.d. 0.3 mm × 50 m long) suspension coated with OV-101 was prepared in basically the same way described by McKeag et al.[18] The column temperature was programmed from 40 to 250 °C at a rate of 2 °C/min. Here, hydrogen was used as carrier gas at a flow rate of 50 mL/min at the pyrolyzer. After splitting by 70:1, the carrier gas flow rate at the capillary column was about 0.72 mL/min. Scavenger gas of 50 mL/min (N_2) was added at the outlet tube just before the FID. The FID was operated at 30 mL/min of hydrogen and 0.4 L/min of air. Sample size around 300 μg was pyrolyzed at 650 °C under the flow of hydrogen carrier gas. The peak assignment of the pyrograms was carried out by direct combination of the capillary gas chromatograph with a mass spectrometer, Shimadzu-LKB-2091. The assignment was supplementally confirmed by comparison of the extensive chromatographic data by Seeger and Barrall[14] and the boiling point data from Beilstein's Handbuch der Organische Chemie. The peak area of the resulting pyrograms was integrated by an integrator (Shimadzu, Chromatopack E-1A).

Results and Discussion

As shown in Figure 2, the gross pyrogram of PE without hydrogenation (A) consists of serial triplets corresponding to n-alkanes, n-alkenes, and α,ω-alkadienes. On the other hand, after hydrogenation these triplets are simplified into singlets of the corresponding n-alkanes. The slighly preferential formation of C_{10} and C_{14} alkanes suggests that the intramolecular radical transfers to 9th and 13th are favored among the possible radical transfers. This phenomenon is explained by the coiling or back-biting process through pseudocyclization steps.[14,19-21] However, Seeger et al.[21] reported that beyond C_{11}, almost noncharacteristic random cleavages are predominant for PE.

Figure 3 shows the high-resolution pyrograms of various PE and the ethylene–α-olefin copolymers taken by pyrolysis–hydrogenation technique at an elevated sensitivity. The minor peaks between the serial main peaks of n-alkanes are mostly attributed to isoalkanes which are closely associated with the branching structures in polymer backbones. For example, the relatively strong minor peaks

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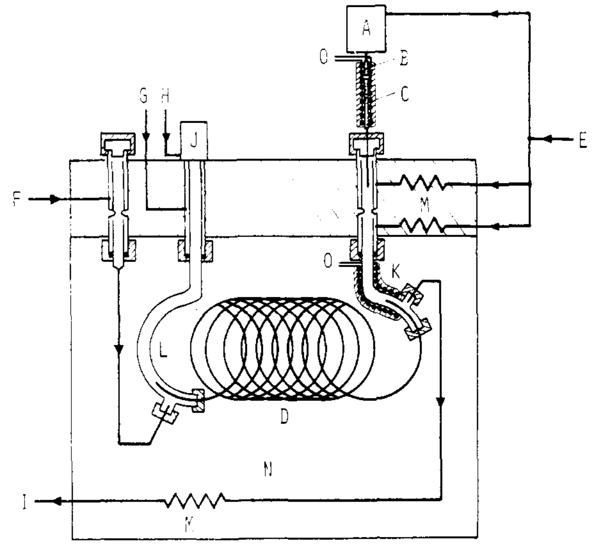


Figure 1. Schematic flow diagram for pyrolysis–hydrogenation glass capillary gas chromatograph: A, pyrolyzer; B, precut column; C, hydrogenation catalyst column; D, glass capillary column; E, carrier gas inlet (H_2); F, scavenger gas inlet (N_2); G, hydrogen inlet; H, air inlet; I, vent; J, FID; K, splitter; L, outlet glass tubing; M, resistance tube; N, column oven; and O, power supply for heater.

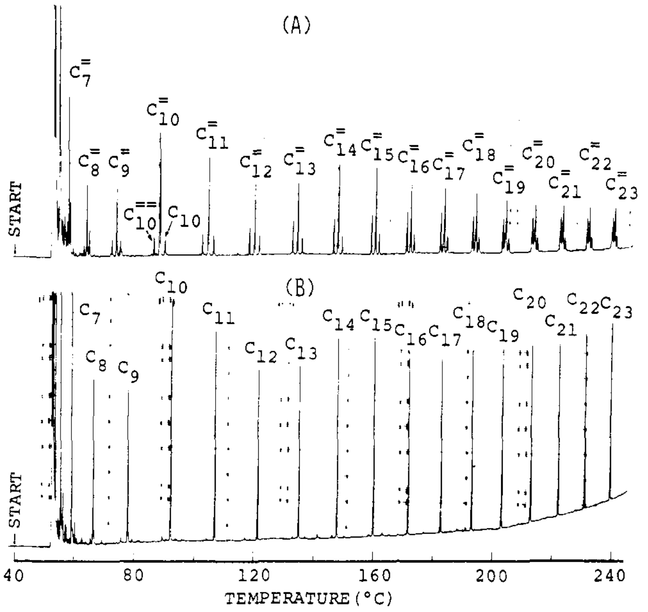


Figure 2. High-resolution pyrograms of HDPE sample. HDPE synthesized by a low-pressure process (A) without hydrogenation and (B) after hydrogenation: C_{10}, n-C_{10}-alkane, $^{=}C_{10}$, C_{10}-α-olefin; $^{==}C_{10}$, C_{10}-α,ω-diolefin.

of 2-methylalkanes (2-M), 3-methylalkanes (3-M), and 5-methylalkanes (5-M) are characteristic of P(E-*co*-P), P(E-*co*-butene), and P(E-*co*-hexene), respectively. As summarized in Table I, various degradation products are formed from the moiety of the isolated short branches. These products mentioned above, however, are mostly formed through the β scissions from the tertiary carbon where the branches originate since both α and β bonds are more susceptible to thermal cleavages than the other bonds, but the α-bond cleavages yield only *n*-alkane. Here, the cleavages in short branches and the formation of dialkyl isoalkanes were not taken into consideration.

In order to develop more detailed discussion, the typical portions of the expanded pyrograms between C_{10} and C_{11} are illustrated in Figure 4. The minor satellite peaks around the *n*-alkanes (peaks A–K) are almost noncharacteristic of the differences in the short branches. Although these might be attributed to cycloalkanes and residual olefines, they do not interfere with the characteristic peaks associated with the short branches.

From the pyrogram of P(E-*co*-P), the intensities of the 3-M, 4-M, and 5-M alkane peaks are almost comparable and about half of that for the 2-M alkane. Therefore, relative probabilities (*P*( )) of the cleavages along the backbone can be regarded as $P(\beta) \doteqdot 2P(\gamma) \doteqdot 2P(\delta) \doteqdot 2P(\epsilon)$. Similarly, from the associated peaks on the pyrogram of P(E-*co*-butene), $P(\beta) \doteqdot 2P(\gamma) \doteqdot 2P(\delta) \doteqdot 2P(\epsilon)$ can be assumed. However, from the pyrogram of P(E-*co*-hexene), the contribution from the other short branches along the ethylene sequences (methyl and ethyl) is overlapping because of the small 1-hexene content (1.5 wt %), but the

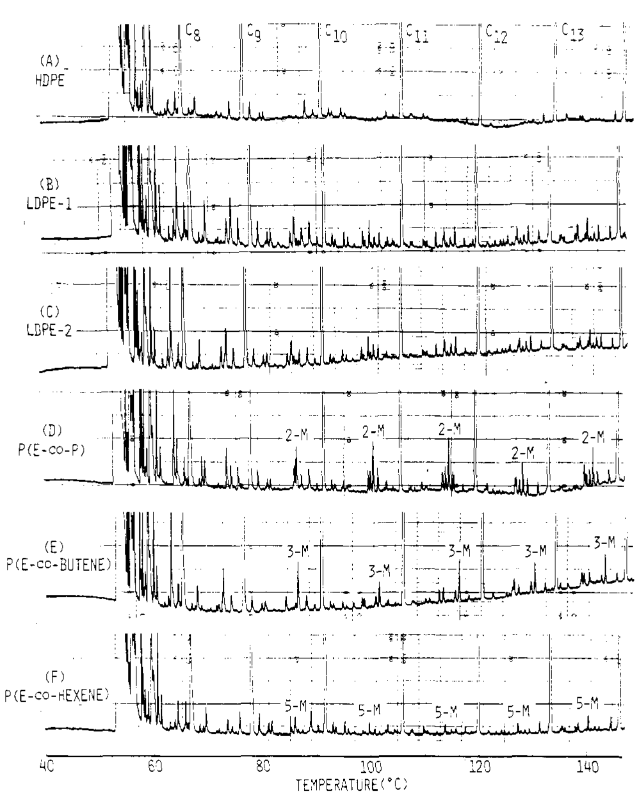
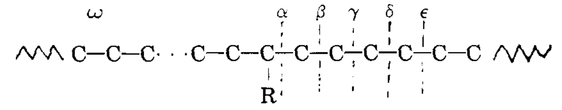


Figure 3. High-resolution pyrograms of polyolefins: (A) HDPE by a low-pressure process; (B and C) LDPE by a high-pressure process; (D, E, and F) ethylene–α-olefin copolymers, C_{10}, n-C_{10}-alkane; 2-M, 2-methylalkanes; 3-M, 3-methylalkanes; 5-M, 5-methylalkanes.

Table I
Possible Fragmentation Products from the Moiety of Branching Structures in PE

short branches in PE[a]	degradation products formed through the scission accompanied by α, β, γ, δ, and ε cleavage[a]				
	α	β	γ	δ	ε
methyl (*n* = 1)	*n*	2-M	3-M	4-Pr	5-M
ethyl (*n* = 2)	*n*	3-M	3-E	4-E	5-E
propyl (*n* = 3)	*n*	4-M	4-E	4-Pr	5-Pr
butyl (*n* = 4)	*n*	5-M	5-E	5-Pr	5-B

[a] scission type:



(R = $(CH_2)_{n-1}CH_3$). N, *n*-alkanes; 2-M, 2-methylalkanes; 3-M, 3-methylalkanes; 4-Pr, 4-propylalkanes.

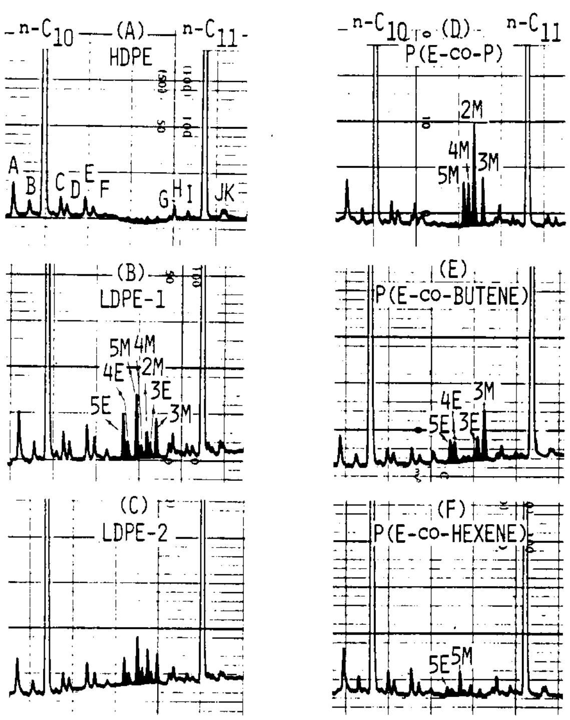


Figure 4. Expanded high-resolution pyrograms of polyolefins around C$_{10}$–C$_{11}$. Sample: the same as shown in Figure 3. A, B, ..., K: noncharacteristic saterite peaks: n-C$_{10}$, decane; n-C$_{11}$, undecane; 2-M, 2-methyldecane; 3-M, 3-methyldecane; 4-M, 4-methyldecane; 5-M, 5-methyldecane; 3-E, 3-ethylnonane; 4-E, 4-ethylnonane; 5-E, 5-ethylnonane.

relatively strong 5-M alkane peak is quite characteristic of the butyl branches which are additionally introduced by the comonomer (1-hexene).

HDPE synthesized by a medium-pressure process gave an almost identical pyrogram with that of HDPE by a low-pressure process. On the other hand, from the comparison of the pyrograms of LDPE and HDPE, it is quite obvious that the former have more short branches than the latter. Although methyl, ethyl, and butyl branches have been characterized to exist as the main short branches, it is recognized that relative abundances can vary over a wide range depending on the polymerization conditions. The total methyl branches for LDPE-1 and -2 observed by the IR method are almost capable, 28.5 and 29.3 per 1000 carbons, respectively. However, it is very interesting to notice that significant differences can be observed in the relative peak intensities characteristic of the short branches (Figure 4B,C). Simulating the corresponding peak intensities on the pyrograms of the LDPE's using the data of the model copolymers mentioned above, the relative abundances of the short branches are estimated as butyl > ethyl > methyl for LDPE-1 and butyl > ethyl ≑ methyl for LDPE-2. These data suggest that the commercial LDPE-2 might be synthesized in the presence of a small amount of propylene to regulate the physical properties. That is to say, the LDPE-2 might belong to an ethylene–propylene copolymer. Such type of modification is widely known in the industrial polymerization of ethylene.[22]

In this work, we demonstrated the effectiveness of the high-resolution pyrograms obtained with various polyolefins by the pyrolysis–hydrogenation glass capillary gas chromatography for characterization of the branching microstructures. By this method, the nature and the relative amount of the short branches in PE, and the minor comonomer components in ethylene–α-olefin copolymers, can easily be qualified. If complete identifications of the minor peaks appearing between the n-alkanes are made and the cleavage probabilities around the branching structures are experimentally determined using well-characterized model polymers, a rapid and highly sensitive method for estimating the total amount of branches and their relative abundances could be established. Further work along this line is currently in progress.

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