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Investigations of the thermodegradation of ethylene–α-olefin copolymers by pyrolysis-gas chromatography (Py-GC)

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Abstract

The thermodegradation of several ethylene–α-olefin copolymers, where α-olefin was butene-1, hexene-1, octene-1 or 4-methyl-1-pentene, was investigated by the pyrolysis-gas chromatography (Py-GC) technique. The study of the various pyrograms has allowed the discrimination of these polyethylenes (PEs) produced from different catalyst systems and processes. It was shown that the pyrolysis products could be classified into two families depending upon the type of the thermal degradation mechanism. In this way, it was demonstrated that, first, the nature and the amount of the comonomer, and, second, the long chain branching are the two structural features controlling the pyrolysis process. The quantitative ratio of these two families is a promising tool to classify the various polyethylene categories. In addition, a statistical approach was applied to discriminate the different PE families. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Ethylene–α-olefin copolymers; Pyrolysis-gas chromatography; Statistical analysis

1. Introduction

The knowledge of physical and structural features of synthetic polymers is fundamental to understanding the properties of materials and their processing behaviour. In this respect, the study of the molecular structure is a key issue, particularly the nature, the amount and the distribution of branches along the polymer backbone. Most of the techniques used in polyolefin analytical departments (DSC, SEC and rheology) and those described in the literature [1–3] for characterisation of chain branching are well-known methods, essentially ^1H and ^{13}C NMR and IR spectroscopies.

Nevertheless, it has been recognised that pyrolysis-gas chromatography (Py-GC) is a powerful method to characterise polyolefin microstructure and particularly in the case of polyethylene (PE). Most of the studies describe the use of model copolymers to identify and quantify short chain branching [4–13], whereas only a few articles deal with the long chain branching analysis [14,15]. This second item is currently a very important area of interest.

In this article, the thermodegradation of ethylene — α-olefin (C_2–C_n) copolymers where C_n is butene-1, hexene-1, octene-1 or 4-methyl-1-pentene is presented. PE types such as low density polyethylene (LDPE), high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) are synthesised with different catalyst systems and processes. According to the pyrolysis products, it is demonstrated how various PE can be discriminated by comparison of characteristic peaks on the corresponding pyrograms. A statistical analysis has been applied to emphasise the discrimination of different species as a function of pyrogram peaks.

2. Experimental

2.1. Samples

The tests were performed on polyethylene samples that had been synthesised by several catalyst systems to provide typical properties. The products studied were LDPE, HDPE and LLDPE. The LLDPE 1–10 include four comonomer types: butene-1 (C_4), hexene-1 (C_6), octene-1 (C_8) and 4-methyl-1-pentene (4MP1). They have been analysed by ^1H and ^{13}C NMR, IR, SEC. All samples and their characteristics are presented in Table 1.

2.2. Equipment and Py-GC conditions

The experiments were performed with a Fischer GSG Curie-Point pyrolyser (model AS24). The high-frequency

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Table 1
Physical characteristics of studied polyethylene and the percentage of “light compounds” (LC) and “heavy compounds” (HC) constituting the pyrogram

Sample	Catalyst system	Process	Melt index[a] (g/10 min)	Density (g. cm^{-3})	Comonomer[b]				M_w (10^{-3}) (g. mol^{-1})	MWD	LC[c] wt.(%)	HC[c] wt.(%)
					C_4	C_6	4MP1	C_8				
LDPE 1	Radical	High pressure	2.00	0.921	NC[d]	NC[d]	NC[d]	NC[d]	115	6.8	0.707	0.293
LDPE 2	Radical	High pressure	0.89	0.920	NC[d]	NC[d]	NC[d]	NC[d]	130	6.0	0.717	0.283
HDPE 1	Ziegler	Gas phase	6.00	0.932	12.0	—	—	—	66	4.0	0.195	0.805
HDPE 2	Ziegler	Gas phase	78.00	0.946	6.3	—	—	—	33	3.5	0.063	0.937
HDPE 3	Ziegler	Gas phase	26.00	0.951	3.8	—	—	—	43	3.5	0.058	0.942
HDPE 4	Ziegler	Gas phase	4.00	0.949	2.3	—	—	—	74	4.0	0.130	0.870
HDPE 5	Ziegler	Gas phase	7.50	0.957	0.5	—	—	—	62	3.5	0.066	0.934
LLDPE 1	Ziegler	Gas phase	2.80	0.917	22.8	—	—	—	82	3.5	0.239	0.761
LLDPE 2	Ziegler	Gas phase	0.72	0.924	14.8	—	—	—	123	3.5	0.229	0.771
LLDPE 3	Ziegler	Gas phase	4.00	0.930	12.4	—	—	—	74	3.5	0.207	0.793
LLDPE 4	Ziegler	Gas phase	0.60	0.918	—	—	14.8	—	130	4.0	0.541	0.459
LLDPE 5	Ziegler	Gas phase	0.85	0.923	—	—	14.3	—	117	4.0	0.668	0.332
LLDPE 6	Ziegler	Gas phase	2.90	0.917	—	22.0	—	—	81	4.0	0.499	0.501
LLDPE 7	Ziegler	Gas phase	0.95	0.917	—	19.0	—	—	106	4.0	0.320	0.680
LLDPE 8	Metallocene	Gas phase	0.60	0.920	—	11.0	—	—	96	2.1	0.243	0.757
LLDPE 9	Metallocene	Solution	1.16	0.917	—	—	—	15.6	107	2.5	0.580	0.420
LLDPE 10	Ziegler	Solution	1.21	0.917	—	—	—	11.9	111	3.5	0.547	0.453

[a] 2.16 kg/min.
[b] Branch/1000 C.
[c] LC and HC are light and heavy compounds, respectively.
[d] NC = Not calculated.

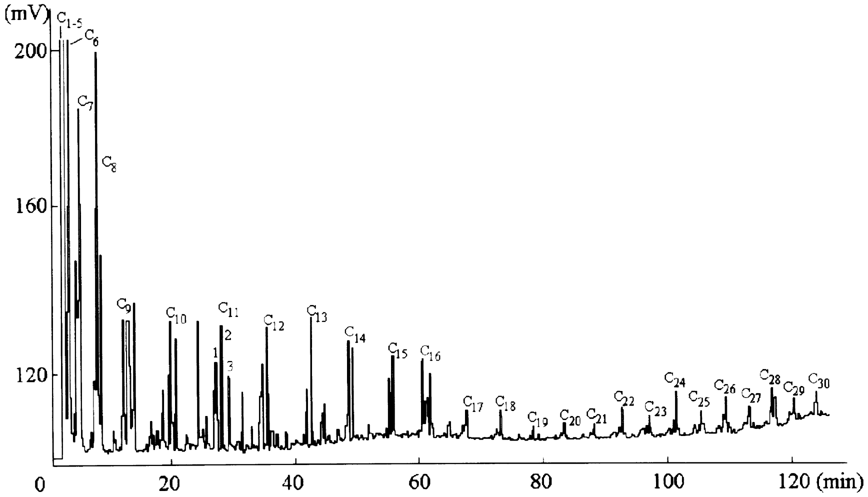


Fig. 1. Pyrogram resulting from the thermal degradation of a low density polyethylene (LDPE 2) at 670°C showing a homologous triplets series of aliphatic hydrocarbons. Each triplet consists of 1: the α,ω-diene; 2: the α-olefin and 3: the n-alcane at each carbon number.

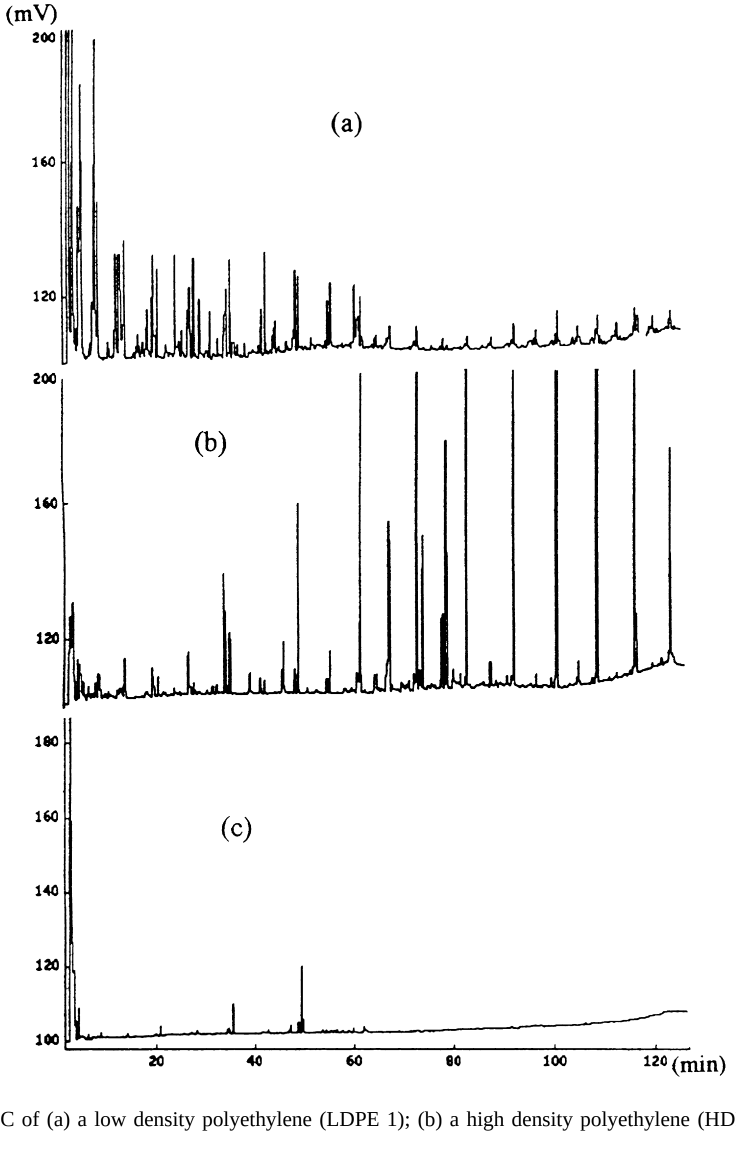


Fig. 2. Pyrograms obtained at 670°C of (a) a low density polyethylene (LDPE 1); (b) a high density polyethylene (HDPE 5) and (c) a low density linear polyethylene (LLDPE 5).

unit was directly connected to a Chrompack CP 9001 gas chromatograph equipped with a flame ionisation detector (FID) and a fused-silica capillary column coated with chemically bonded cross-linked methylsilicone (Restek BPX5:30 m × 0.25 mm i.d., 0.25 μm film thickness).

A piece of polymer film (weight 2.5 mg) was introduced into a ferromagnetic rod (85 × 0.5 mm) equipped with a cylindrical sample holder. This film of about 100 μm thickness has been melt-pressed at a temperature of 150°C. The sample was pyrolysed at 670°C for 10 s under a flow of helium carrier gas. A split of 1:30 was maintained at the capillary injection port.

The volatile products were separated on the column with a temperature program of 40°C for 2 min to 280°C for 5 min at a rate of 2°C/min.

Identification of pyrolysis products was achieved by comparison with the retention times of a linear paraffin mix.

3. Results and discussion

3.1. Thermodegradation of PE

As an example, Fig. 1 illustrates a typical pyrogram for LDPE thermodegraded at 670°C. The characteristic components of pyrolysed PE are a series of aliphatic hydrocarbons (triplets consisting of α,ω-dialkenes, alkenes and *n*-alkanes) from C_5 (below C_5 compounds probably exist but are not separated) to C_{30}. These products are the result of C–C homolytic chain scission of the polymer. These observations are in good agreement with the results published in the literature. The degree of branching is an important factor in the PE degradation mechanism. Wall and Flynn [16] have shown that the decomposition of branched polymers is slightly faster than for the unbranched forms. Moreover, the breakage of the polymer backbone from side chains is increasingly favourable with longer branch length and especially up to four carbons [4].

From these results, the assumption has been made that several factors could influence the pyrolysed products, e.g. the type of monomer and the comonomer sequence distribution. We have chosen several PE with different comonomers and from various catalyst systems in order to investigate this phenomenon.

3.2. Pyrolysis of three different PE

The pyrograms of three different PE (LDPE 1; HDPE 5; LLDPE 5) are presented in Fig. 2 for comparison. It can be observed that in the thermodegradation of LDPE 1 all triplets are present but the most important proportion is located in the light products. This phenomenon may be explained by the LDPE structure which is composed of many different short branches (methyl, ethyl, propyl, butyl, etc.), long chain branches and also a low number of cross-linkages. All these branch types are favourable to breakage. However, high oligomers, in lower proportion, can be observed in the pyrogram indicating that LDPE 1 contains unbranched chain segments as expected for such a PE type. This result is in good agreement with those of the literature [4,6,9].

HDPE 5 is a PE homopolymer and as such is considered as our reference product. Its thermodegradation essentially provides high oligomers as main products and a very low proportion of light compounds. In the relative absence of long or short chain branching, the backbone breakage of HDPE 5 is random. This result confirms our initial hypothesis.

While the light volatile products are almost non-existent in HDPE 5, in the case of the LLDPE 5, they represent the majority of the pyrogram. This can be explained by the presence of comonomer and its chemical structure. The 4MP1 comonomer has a tertiary carbon in the branch, which will preferentially lead to scission [4,17]. In order to broaden these observations, we can compare now the influence of the comonomer nature and its concentration for each copolymer family.

3.3. Influence of the comonomer

In order to compare and understand the influence of comonomers, we have introduced a differentiation criterion: we have chosen to separate pyrogram peaks into two classes. These two families have been differentiated by a chain length limit, allowing the terminology “light compounds” (LC) and “heavy compounds” (HC). LC are defined as compounds with a low molecular weight (nine or less carbons) whereas HC represent oligomers (between 10 and 30 carbons) which are more characteristic of the polymer structure. The quantitative determination of these two groups is a first approach to discriminate polymer families.

In Table 1, the proportion of LC and HC are given for each polymer type. As expected, the values differ with the nature and the amount of comonomer. It can be seen that LDPE provide about 70% of LC whereas only 5% are

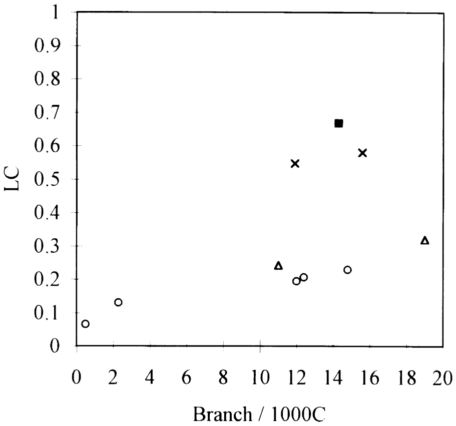
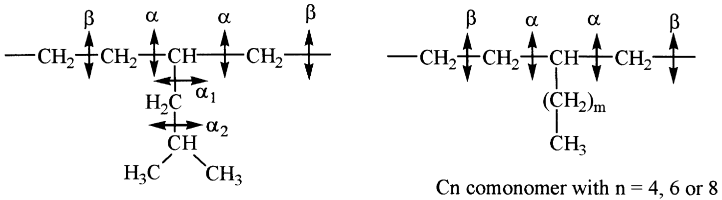


Fig. 3. Variation of low compound (LC) concentration in function of branch per 1000 carbons in copolymers (○: LL and HDPE C_2–C_4; ■: LLDPE C_2–4MP1; △: LLC_2–C_6 ZN; ×: LLDPE C_2–C_8:)



4MP1 comonomer

Cn comonomer with n = 4, 6 or 8
where m = 0, 2 or 6

observed in case of the HDPE. The LC variation is not significant within the comonomer concentration range that we have considered for the HDPE samples. This observation is similar for the LLDPE samples containing C_4 comonomer. In spite of a different comonomer (C_4 and C_6) but with the same amount, LLDPE 1 and 8 give the same results. This observation could be explained by a different catalyst system.

The pyrograms of LLDPE containing 4MP1 comonomer present an important fraction of LC. However, the concentration of the 4MP1 group has only a low impact in the LC formation. Further, we can observe that this comonomer within four carbons side chain can have various fragmentations (α_1, α_2, α, β) induced by the tertiary carbons.

From these results, we can deduce that copolymers with side chain branches up to C_8 are only degraded by their backbone (α and β scission) and the increase of the comonomer amount gives a proportional scission. In this case, it is the side chain length of the comonomer which has an influence on the degradation. By increasing the side group length (C_4, C_6, and C_8), the thermal degradation (α and β) is more and more favoured. This phenomenon is represented by the increased amount of LC (Table 1). The chemical nature of the comonomer also has a great influence. The thermal degradation behaviour of 4MP1 comonomer is extremely different than that of the other C_2–nC_6 copolymers: the existence of a tertiary carbon into the comonomer induces an internal scission of the side group (the more favourable being α_2) as shown in the scheme above which explains the high percentage of LC (about 75%).

We have represented in Fig. 3 the LC variation in function of the branch concentration of copolymers which have the same density and melt index in order to understand the pyrolysis behaviour of each comonomer. This graph shows that the copolymers C_2–nC_n (HD and LL) with C_4 or C_6 comonomer gives the expected results because the LC amount increases with a higher branch level. In contrast, products containing C_8 and 4MP1 groups show a higher LC percentage which confirms their different behaviour in pyrolysis. We can interpret this result as being caused by the C_8 and 4MP1 side branches being degraded.

The molecular weight ($\bar{M}_w$) is another parameter to consider as contributing to the pyrolysis. We can see in Table 1 that the comparison of two copolymers (LLDPE 6 and 7), having a similar density but very different melt index and $\bar{M}_w$, indicates a difference in the LC proportion. The latter is much higher in the case of the LLDPE 6 which has the lower $\bar{M}_w$. From this observation, it could be proposed that the terminal chain group could have an influence on the degradation of the polymer.

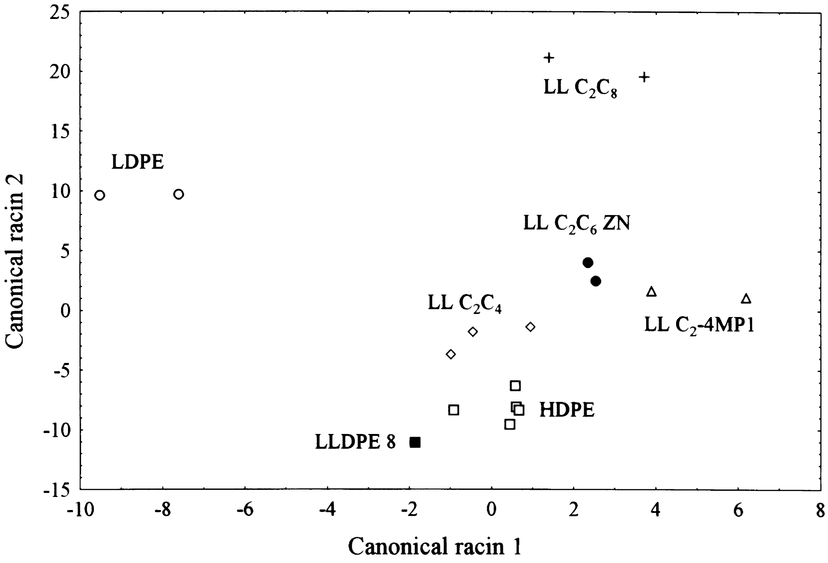


Fig. 4. Discriminant analysis applied to pyrogram data from 17 studied polymers representing seven groups. Canonical variates plot derived from variables (peaks of pyrograms) and resulting of six iterations.

3.4. Statistical analysis

We have observed that, from the peaks of the pyrograms, a statistical analysis allows a good separation of the polymer families according to different properties, such as the kind of catalysis and the comonomer type. The data set is made from the area of selected peaks as variable and from the products as observations. A discriminate analysis was applied to these data from the 18 studied polymers representing seven groups (LDPE 1 and 2; HDPE 1–5; LLC_2–C_4: LLDPE 1–3; LLC_2–C_6 ZN: LLDPE 6 and 7; LLC_2–C_6 metallocene: LLDPE 8; LLC_2–C_8: LLDPE 9–10). The canonical variates, calculated from variables and with six iterations, are plotted in Fig. 4. We can observe that the polymers produced by free radical polymerisation, having a different structure are clearly discriminated. Nevertheless, the statistical analysis shows that the pyrolysis products can give more information: besides the discrimination by monomer type, it is possible to separate families having a different microstructure (C_2–C_4: LL and HD), also the catalysis is another discriminating parameter (LLDPE 8 $\neq$ LLDPE 6 and 7).

4. Conclusion

This study shows that it is possible to discriminate polyethylenes (PEs) synthesised with various catalyst systems and processes by comparing the low molecular weight (LC) and high molecular weight (HC) compounds resulting from their thermal degradation. The two main factors influencing the scission of the backbone are the side chain length and its chemical structure. Further, a statistical analysis allows a deeper interpretation of the results for example the copolymers from different catalyst systems are also separated.

According to these results, we suggest that, with a similar approach, it will be possible to extrapolate this differentiation tool to PE materials essentially based on long chain branching features.

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