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APPLICATION OF PYROLYSIS–CAPILLARY GAS CHROMATOGRAPHY TO THE CHARACTERIZATION OF POLYETHYLENE

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SUMMARY

Two modifications of Curie-point pyrolysis-hydrogenation-gas chromatography of polyethylene with wall-coated (squalane) open-tubular columns are described. The off-line method with isothermal chromatography is applied for identification of isoalkanes formed from branched units of polymer. The on-line method with temperature-programmed chromatography is used for quantitative analysis. The area percentage of isoalkanes identified by Kováts' indices and their ratio to n-alkanes are employed to distinguish between high- and low-density polyethylene.

INTRODUCTION

Pyrolysis–gas chromatography (PGC) of polyethylene (PE) has been practised for more than twenty years, not only for analytical purposes[1–4] but also for elucidation of the chemical structure of PE[5–17]. Various modes of pyrolysis have been applied such as off-line decomposition in evacuated glass ampoules[1,9] and in tube ovens[14], but more frequently on-line destruction in heated tubes[2–5,7,12,13], on ribbons[15,16], in filament coils[6,8] and Curie-point pyrolyzers[10,11]. The volatile pyrolytic products have been separated in packed columns[1–3,7,10,12–16], support-coated open-tubular columns[11,15] and wall-coated open-tubular (WCOT) columns[4–6,8,9]. The identification of individual fragments has been simplified by catalytic hydrogenation of products prior to their entering the separation column[2–4,6,8,10,12,13,15]. The above methods have been designed for the analysis of highly volatile hydrocarbons C_1 to C_5 (refs. 1, 3, 7, 10 and 11), the main products between C_5 and C_{10} (refs. 2, 12, 13, 15 and 16) or for the determination of the distribution of fragments in the range C_5–C_{20} or higher[4–6,8,14].

The fundamental PGC study on the chemical structure of PE was performed by Seeger and Barrall[12]. Their method comprised the identification of isoalkanes formed by splitting of polymer units possessing alkyl branches, and in the theoretical treatment of the results obtained. The chemical structure of PE has also been studied by other physico-chemical methods, especially ^{13}C nuclear magnetic resonance and infrared spectroscopy and γ radiolysis, which are reviewed by Cutler and Hendra[17], Spěváček[18], Browmer and O'Donnell[19], and Randall[20].

On the basis of the previous results it is believed that low density PE is characterized by a relatively high degree of branching (25–50 atoms per 1000 main chain

carbon atoms), consisting mainly of ethyl and butyl groups and a small proportion of longer branches. There is no consensus as to the relative proportions of the branches of different chain length. In high density polyethylene, methyl branches predominate in a concentration ten times lower.

The interpretation of the results of PGC analysis of PE suffers from the lack of a more precise quantitative method based on separation of all characteristic products. We decided to improve the method of Seeger and Barrall[12] by using a more effective WCOT column and a more reproducible Curie-point pyrolyzer. Two modifications are proposed: discontinuous pyrolysis–hydrogenation and GC analysis (off-line PHGC) and a continuous procedure (on-line PHGC). The first system together with isothermal heating of the column served for identification purposes using Kováts' indices; the second together with temperature programmed chromatography was employed for quantitative interpretations.

EXPERIMENTAL

Off-line PHGC

A schematic diagram of the off-line PHGC system is shown in Fig. 1. The trap (7) was cooled by dry-ice. The catalytic oven (4) containing 5% Pt on Chromosorb W (80–100 mesh) was heated to 200° in a stream of hydrogen (15 ml/min). A 2-μl volume of n-pentane was injected through the septum (1). It condensed in the trap and served as a collector for highly volatile products. Then 1.0 $\pm$ 0.1 mg of sample fixed in a loop of ferromagnetic iron wire was inserted in the coil (3) of the Curie-point pyrolyser (PV 400; Phillips, Great Britain). After equilibration the sample was pyrolyzed for 15 sec at 770° and held at this temperature for 30–60 sec to allow the products to pass into the trap. The pyrolysis of new samples was carried out in triplicate to ensure sufficient amounts of products for analysis. Finally, 2 μl of n-pentane were injected to rinse out the remaining products. Both ends of the trap were sealed with a microburner (first the inlet part) and the resulting ampoule was centrifuged to concentrate the solution in the tip of the trap. The tip was then cut off and 1 μl of the solution was injected into the gas chromatograph with the column held isothermally at 100° under nitrogen carrier gas at 100 kPa inlet pressure.
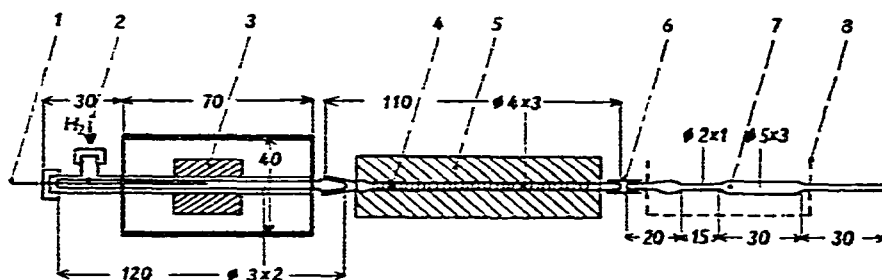

Fig. 1. Diagram of off-line pyrolysis system: 1 = entry port; 2 = hydrogen inlet; 3 = high-frequency coil of Curie-point pyrolyzer; 4 = quartz tube containing 5% Pt on Chromosorb W; 5 = electrical oven heated to 200°; 6 = PTFE connnection tube; 7 = trap; 8 = Al boat with dry-ice. Dimensions are given in mm.

On-line PHGC

A tube with catalyzer was inserted into the injection port of the gas chromatograph with the aid of an adapter (Fig. 2). The entrance coil of the capillary column was wound off and formed into a loop. After cooling the column to room temperature and the loop with dry-ice or liquid nitrogen, the Curie-point pyrolyzer containing 0.1 ± 0.01 mg of the sample in a loop of ferromagnetic wire was connected to the gas chromatograph by penetrating the septum of the injector port with the needle fixed to the pyrolyzer. A stream of hydrogen carrier gas was passed through the pyrolyzer and after a short equilibration the sample was pyrolyzed for 15 sec at 770°. The pyrolyzer was disconnected, the loop cooling system was removed and the column was heated to 100° at a rate of 2.5°/min and an inlet hydrogen pressure of 100 kPa.
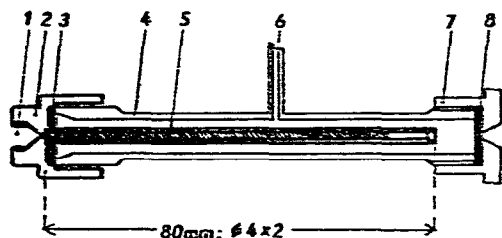

Fig. 2. Adapter for on-line hydrogenation: 1 = connection for capillary column; 2 = brass nut; 3 = silicone rubber seal; 4 = injector of gas chromatograph; 5 = 5% Pt on Chromosorb W; 6 = hydrogen inlet; 7 = septum nut; 8 = septum.

Apparatus

A Fractovap 2201 (Carlo Erba, Milan, Italy) was used for analysis, equipped with a stainless-steel capillary column (45 m × 0.25 mm I.D.). After cleaning with phosphoric acid, water, acetone and benzene, the column was coated with 10% squalane in benzene by a dynamic method. The column reached 65,000 theoretical plates for n-decane under working conditions. The signal from the flame ionization detector (FID) was processed with a Hewlett-Packard 3380 A reporting integrator.

Materials

Low-density PE, Bralen KB 2-11, was obtained from Slovnaft (Bratislava, Czechoslovakia), high-density PE Vestolen A, from Hoechst (Frankfurt/M, G.F.R.). Perkadox SB [bis(α,α'-dimethylbenzyl) peroxide] and Perkadox P-14 [α,α'-bis-(tert.-butylperoxy)-diisopropylbenzene] were from Noury Van Der Lande (Deventer, The Netherlands).

RESULTS AND DISCUSSION

For identification of isoalkanes in hydrogenated pyrolytic products, the laborious off-line PHGC was used in order to keep to the same analytical conditions at which the published Kováts' indices were obtained (instantaneous introduction of sample, isothermal heating, nitrogen as carrier gas). Published Kováts' indices obtained on isoalkane standards[21–25] are compared in Table I with experimental values for pyrolytic products obtained using both procedures. There is good agreement between literature values and experimental values obtained by the isothermal proce-

TABLE I

COMPARISON OF PUBLISHED AND EXPERIMENTAL KOVÁTS' INDICES

No.	Isoalkane	Lit. values					Exptl. values	
		21 (60°)	22 (60°)	23 (86°)	24 (80°)	25 (100°)	Isothermal	Programmed
1	2M6	—	668.8	667.2	—	667	—	668.8 ± 0.3
2	2M7	—	765.0	765.2	—	766	765.2 ± 0.6	762.0 ± 0.6
3	3M7	—	772.6	773.5	—	775	773.4 ± 0.4	769.5 ± 0.4
4	4M8	863.3	—	863.1	863	864	863.7 ± 0.4	862.8 ± 0.1
5	3E7	867.4	—	—	868	869	869.3 ± 0.4	867.2 ± 0.1
6	3M8	870.8	870.4	—	871	872	871.9 ± 0.3	870.5 ± 0.3
7	4E8	951.5	—	—	952	—	952.2 ± 0.2	951.4 ± 0.3
8	5M9	957.4	—	—	958	—	957.9 ± 0.2	957.4 ± 0.4
9	2M9	963.9	—	—	964	—	965.0 ± 0.2	964.0 ± 0.3
	3E8	964.0	—	—	—	—		
10	3M9	969.6	—	—	970	—	970.5 ± 0.2	969.7 ± 0.3

* The first number for each isoparaffin indicates the position of the side chain and the last the length of the main chain in C atoms. The letters denote the kind of substituent (M = methyl, E = ethyl).

dure. However the retention indices obtained by the temperature-programmed procedure differ significantly, especially for lower isoparaffins. The reproducibility of retention indices from both procedures is very good and is represented by a relative error of only ±0.04%. The advantage of temperature-programmed chromatography is the possibility of analyzing low-boiling fragments, such as pentanes (on cooling with dry-ice) and butanes (on cooling with liquid nitrogen).

In the isothermal procedure the early peaks are too sharp and poorly separated and the later peaks are too broad for quantitative interpretation. The temperature-programmed procedure is therefore not only more suitable for quantitative purposes but is also simpler and time-saving.

Pyrograms of low-density PE (upper line) and high-density PE (lower line) are shown in Fig. 3 with the peak identification as in Table I. From simple visual comparison, it is evident that some parts of these two pyrograms are similar, but other parts differ considerably. The predominant peaks represent n-alkanes, the high peaks in the region of low-molecular-weight fractions (C_6-C_8) belonging to alkylcyclopentanes and alkylcyclohexanes, being products of cyclization of lower oligomers. As with n-alkanes, cycloalkanes are the products of scission of main polymer chains and are not characteristic for distinguishing between high- and low-density PE. For this purpose only the amount and distribution of individual monosubstituted paraffins is characteristic. Dialkylparaffins were not found in significant amounts.

In the same way we analyzed a number of different samples of PE, either as received or as transformed by cross-linking or by temperature and electrical aging. Owing to the lack of pure standards, we evaluated the amounts of individual isoalkanes as their area percentage and the sum of all as area percentages relative to all n-alkanes in the range C_6-C_{10}. The results are in Table II.

It is evident that low- and high-density PE differ substantially not only in the total amounts of isoalkanes but also in their distribution. In the former, 3-methyl-
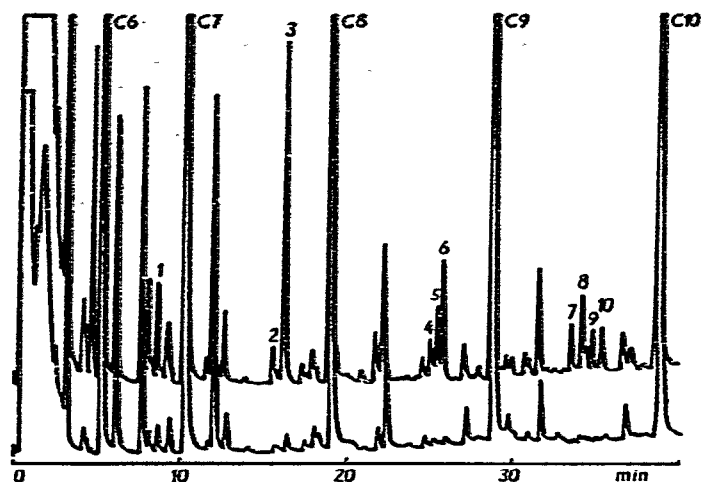
Fig. 3. Pyrograms of low density (upper line) and high density (lower line) PE. For conditions see Experimental; for identification of peaks see Table I.

TABLE II

AREA PERCENTAGE OF ISOALKANES IN PYROLYTIC PRODUCTS AND THEIR AREA SUMS RELATIVE TO n-ALKANES

Samples: 1 = low-density PE, as received; 2 = low-density PE cross-linked with 2% Perkadox SB; 3 = low-density PE cross-linked with 2% Perkadox P-14; 4 = low-density PE, aged for 300 h at 90°; 5 = low-density PE, aged for 300 h at 90° and 2000 V; 6 = cable insulation from cross-linked low-density PE, as received; 7 = cable insulation as above, aged for 9780 h at 50.5 kV; 8 = high-density PE, as received; 9 = high-density PE, cross-linked with 2% Perkadox SB.

No.	3M7	3M8	2M6	3E7	5M9	4E8	3M9	4M8	2M7	3E8, 2M9	Isoalkanes relative to n-alkanes
1	44.3	14.6	11.2	7.2	6.6	4.0	3.7	3.6	2.8	2.0	11.86
2	43.6	12.2	10.4	8.0	6.8	5.0	4.0	3.2	2.8	3.8	12.85
3	45.6	12.6	11.6	8.4	5.6	3.7	3.6	1.6	3.9	5.6	14.70
4	44.6	11.6	12.2	7.5	5.3	4.3	3.5	4.1	3.4	3.6	10.70
5	39.9	12.5	8.3	7.8	9.4	5.0	3.9	5.6	4.1	3.5	11.59
6	37.8	13.8	8.1	6.4	10.7	5.0	4.1	5.8	4.3	3.3	12.58
7	38.2	12.7	9.1	7.2	8.8	5.3	4.6	6.1	4.2	3.7	12.29
8	19.6	9.8	33.0	8.0	11.6	—	—	13.4	4.5	—	1.12
9	22.6	8.7	36.5	3.5	4.3	—	1.7	15.6	6.1	0.9	1.15

alkanes are predominant, whereas in the latter 2-methylhexane is the dominant peak. Considering the probability of formation of isoalkanes, in terms of their side chains, we may suppose that in low-density PE the presence of methyl, ethyl and butyl groups is equally probable (each *ca.* 30%) and remaining groups are propyl, amyl and higher alkyls. If we then allow the scission of side chains, the butyl groups must predominate. In high-density PE the probability of the formation of methyl side groups is considerably greater (over 40%) than the remainder, which are mainly ethyl and butyl groups.

The small difference in total amounts of isoalkanes and cross-linked PE is

surprising. It may be explained either by a low number of cross-linkage between linear macromolecules, or by a preference for breaking of cross-linkages during pyrolysis.

During thermal and electrical aging of PE, loss of the side chain was expected. However, the results in Table II show that this reaction made a negligible contribution. During aging, other chemical reactions may occur, such as statistical chain scission, propagation and cross-linking. None of these reactions may be observed by PGC of the remaining polymer, and thus the analysis of the volatile reaction products is recommended.

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