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## THE PYROLYSIS CAPILLARY GAS CHROMATOGRAPHY OF SOME POLYMERIC MATERIALS

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Received June 1st, 1981

*Dedicated to Professor J. Zýka on the occasion of his 60th birthday.*

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The thermal degradation of industrially manufactured polymers based on polyethylene, polypropylene and polystyrene was studied. The pyrolysis was carried out in a tubular quartz pyrolyzer at 510°C and the products were separated on capillary columns coated with squalane and OV-17 and were identified on the basis of their retention indices.

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At the present, pyrolysis gas chromatography is a method which is used widely, not only for analysis of non-volatile materials such as plastics, but also for dyes, pharmaceuticals, bacteria, *etc.*

Pyrolytic degradation is not an arbitrary process, but one which can, in principle, be predicted on the basis of thermodynamic and kinetic data. It is, however, very difficult and mostly experiments must be carried out, especially if commercially manufactured polymers, which contain a number of additives, are to be analyzed.

The technique of pyrolysis gas chromatography and especially the construction of pyrolyzers have received a great deal of attention, *e.g.*<sup>1-5</sup>. The products must generally be identified by the GC-MS combination, but it is sometimes possible, as was shown in an earlier work<sup>6</sup>, to identify the substances using the retention indices measured with sufficient precision on a capillary column and comparing them with the values published in the literature.

The reproducibility, especially between laboratories, remains a problem<sup>7,8</sup>. It depends primarily on the type of pyrolyzer and on the experimental conditions, *i.e.* pyrolysis temperature, size and homogeneity of the samples, method of connecting the pyrolyzer to the chromatographic column and separation conditions. All these parameters must be controlled and measured with great precision.

A great deal of attention has been paid to the pyrolysis of plastics<sup>9-15</sup>. Primarily the mechanism of thermal degradation of polymers has been studied. With copolymers, primarily the arrangement of the monomer units in the chain has been considered. This work is concerned with studying the thermal degradation of some industrial plastics based on polyethylene, polypropylene and polystyrene by pyrolysis capillary gas chromatography.

TABLE I

Products of the thermal decomposition of polyethylene Bralen RB 0323. Pyrolysis temperature 510°C, squalane, column temperature 70°C

Peak	Retention index <i>I</i>	Standard deviation <i>s</i> <sup>a</sup>	Product
1	182	10.3	methane, ethylene, ethane
2	300	8.2	propene, propane
3	382	3.6	1-butene
4	449.4	2.3	3-methyl-1-butene
5	463.6	1.7	1,4-pentadiene
6	480.4	1.2	1-pentane
7	500	—	pentene
8	516.8	0.7	1- <i>trans</i> -3-pentadiene
9	538.5	0.6	2,2-dimethylbutane
10	540.0	0.8	—
11	552.1	0.3	4-methyl-1-pentene
12	562.8	0.5	1,5-hexadiene
13	582.5	0.3	1-hexene
14	592.4	0.2	3-hexene
15	600	—	hexane
16	612.8	0.3	1,3-hexadiene, 2-methyl- <i>trans</i> -2-pentene
17	630.6	0.7	2,3,3-trimethyl-1-butene
18	640.8	0.6	benzene
19	645.3	0.8	3-methyl-1-hexene
20	654.1	0.3	4-methyl- <i>trans</i> -2-hexene
21	661.6	0.7	1,6-heptadiene, cyclohexane
22	670.9	0.6	2,3-dimethylpentane
23	679.6	0.6	2-methyl-1-hexene
24	682.6	0.4	1-heptene
25	700	—	heptane
26	708.8	0.2	—
27	712.9	0.5	1,3-heptadiene
28	717.9	0.3	methylcyclohexane, 2,2-dimethyl- <i>cis</i> -3-hexene
29	731.0	0.4	2,4-dimethylhexane
30	734.3	0.2	2,2,3-trimethyl-1-pentane
31	740.8	0.1	2,3-dimethyl-1-hexene
32	752.5	0.7	2-methyl-3-heptene, 2,3,4-trimethylpentane
33	761.1	0.1	2-methyl-3-ethylpentane
34	765.3	0.4	2-methylheptane
35	776.5	0.3	2,2,5-trimethylhexane
36	779.4	0.5	2-methyl-3-ethyl-2-pentene 2-methyl-1-heptene
37	781.5	0.3	1-octene

TABLE I  
(Continued)

Peak	Retention index <i>I</i>	Standard deviation $s^a$	Product
38	800	—	octane
39	812.6	0.4	1,3-octadiene
40	823.4	0.4	—
41	835.6	0.2	—
42	847.6	0.3	—
43	863.4	0.4	—
44	873.5	0.4	—
45	878.5	0.1	—
46	881.0	0.3	1-nonene
47	900	—	nonane
48	912.8	0.7	1,3-nonadiene

<sup>a</sup> Standard deviation for  $n \geq 5$ .

## EXPERIMENTAL

### Chemicals

Pentane, *p.a.* (Laborchemie Apolda, GDR), hexane, benzene, toluene, all *p.a.* (Lachema, Brno), heptane *p.a.* (Loba-Chemie, Vienna, Austria), octane *p.a.* (Phillips, Netherlands), nonane, pure chemical (REACHIM, USSR), decane, undecane (Applied Science Lab., USA). Squalane, OV-17 (Carlo Erba, Italy) The following polymers were used: polyethylene—Bralen RB 0323 (powder, granules) (Slovnaft, Bratislava, Czechoslovakia), polypropylene — Mosten 52 492 (granules, plates), Mosten 52 517 (granules, plates) (Chemické závody, Litvínov), Tatren TF 411 (powder, granules) (Slovnaft, Bratislava, Czechoslovakia), polystyrenes — Krasten 336 (granules, plates), Krasten 127 (granules, plates) (Kaučuk, Kralupy, Czechoslovakia), Kostil SAN (granules, plates) (Montedison, Italy).

### Apparatus

Measurements were carried out on a Chrom 41 gas chromatograph (Laboratorní přístroje, Prague, Czechoslovakia) with an FID. Two stainless steel capillary columns were used, with a length of 50 m and an internal diameter of 0.2 mm, wetted with squalane and OV-17 stationary phases. The plastics were thermally decomposed in a vertical tubular pyrolyzer with a small internal volume constructed in the laboratory<sup>6</sup>. It consists of a heater and a quartz tube 80 mm long with an internal diameter of 2 mm. The heater is a copper cylindrical block placed in a ceramic mantle; the heating spiral is wound on the surface of this block. The pyrolyzer temperature was controlled by a thyristor regulator and measured with a thermocouple.

TABLE II

Products of the thermal decomposition of polypropylenes. Pyrolysis temperature 510°C, squalane, column temperature 70°C

Peak	Retention index <i>I</i>	Standard deviation <i>s</i> <sup>a</sup>	Product
1	196	13.2	methane, ethane, ethylene
2	300	10.1	propane, propene
3	392	8.2	2-methyl-1-propene
4	438	4.6	3-methyl-1-butene
5	462.8	3.0	1,4-pentadiene
6	482.3	1.8	1-pentene
7	500	—	pentane
8	514.3	1.2	1- <i>trans</i> -3-pentadiene
9	526.9	1.4	1,2-pentadiene
10	538.5	0.8	2,2-dimethylbutane
11	550.2	0.3	4-methyl-1-pentene
12	555.6	0.8	4-methyl- <i>cis</i> -2-pentene
13	560.5	0.2	4-methyl- <i>trans</i> -2-pentene
14	563.5	0.4	1,5-hexadiene
15	580.8	0.9	2-methyl-1-pentene
16	599.2	0.4	2,3-dimethyl-1,3-butadiene
17	612.8	0.2	1,3-hexadiene
19	638.5	0.3	2,4-dimethyl-1-pentene
20	640.9	0.5	benzene
21	653.8	0.6	<i>cis</i> -2- <i>trans</i> -4-hexadiene
22	660.6	0.5	2-methyl-1,4-hexadiene
23	666.9	0.2	cyclohexane
24	679.5	0.3	2-methyl-1-hexene
25	688.2	0.4	3-methyl-3-hexene
26	690.3	0.4	2-methyl-2-hexene
27	697.2	0.3	3-ethyl-2-pentene
28	699.7	0.4	2,4-dimethyl-1,4-pentadiene 3-methyl-3-ethyl-1,3-butadiene
29	707.1	0.1	2,4,4-trimethyl-1-pentene
30	720.6	0.1	2,2-dimethyl- <i>cis</i> -3-hexene
31	728.5	0.2	2,5-dimethylhexane
32	732.4	0.2	2,4-dimethylhexane
33	742.1	0.4	2-methyl- <i>trans</i> -3-heptane
34	748.8	0.2	3,4,4-trimethyl- <i>cis</i> -2-pentene
35	751.7	0.1	2,5-dimethyl-2-hexene
36	759.8	0.3	2,3,3-trimethylpentane
37	761.5	0.4	2-methyl-3-ethylpentane
38	765.1	0.3	2-methylheptan

TABLE II  
(Continued)

Peak	Retention index <i>I</i>	Standard deviation <i>s</i> <sup>a</sup>	Product
39	768.9	0.4	4-methyl-1-heptene
40	781.5	0.4	1-octene
41	790.9	0.4	2,2,4-trimethylhexane
42	800	—	octane
43	804.2	0.2	4,6-dimethyl-1-heptene
44	811.6	0.2	1,3-octadiene
45	816.6	0.3	—
46	821.6	0.4	2,4-dimethylheptane
47	826.6	0.3	2,2-dimethyl-3-ethylpentane
48	835.7	0.8	2,4-dimethyl-1-heptene
49	846.4	0.3	—
50	848.9	0.4	—
51	853.4	0.3	—
52	864.2	0.4	2,3,3,4-tetramethylpentane
53	872.4	0.4	—
54	874.3	0.3	2,2,4,5-tetramethylhexane
55	879.9	0.4	—
56	883.7	0.5	<i>trans</i> -4-nonene, 3,3-diethylpentane
57	892.1	0.4	—
58	896.9	0.3	2-nonene

<sup>a</sup> Standard deviation for  $n \geq 5$ .

The solid polymer samples were sampled using a modified syringe. A steel wire was soldered to the centre of the plunger and passed through the needle; when the plunger was completely pressed in, about 5 mm of the wire protruded from the tip of the needle. The syringe was filled with the carrier gas before filling the needle with the sample.

#### Experimental Conditions

Pyrolysis temperature: 510°C, column temperature: 50, 70, 80 and 100°C, carrier gas flow rate (nitrogen) 0.25 ml min<sup>-1</sup>, hydrogen flow rate 35 ml min<sup>-1</sup>, air flow rate 0.25 ml min<sup>-1</sup>, splitting ratio 1 : 100.

The retention indices (*I*) were calculated on the basis of the retention times of the n-alkenes and retention times and indices of selected standards contained in the pyrolysis products. The relative contents of volatile products *X* (%) were found on the basis of the peak height *h* ( $x_i = 100 h_i / \sum_i h_i$ ).



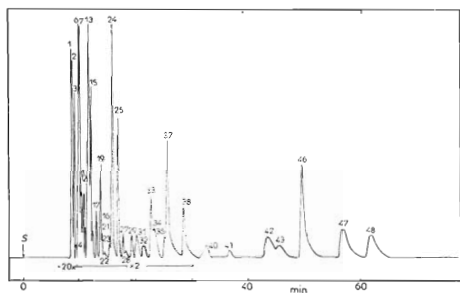


FIG. 1

Chromatogram of the pyrolysis products of polyethylene Bralen RB 0323. Squalane, 70°C, for identification of the peaks, see Table I.

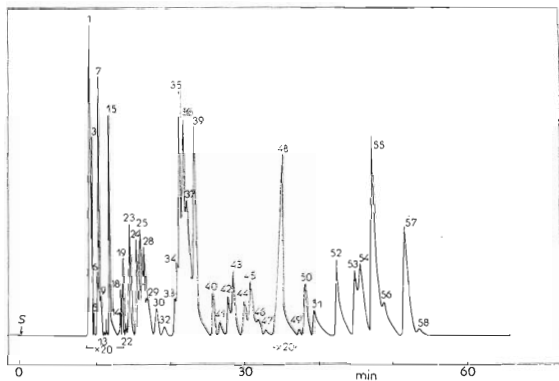


FIG. 2

Chromatogram of the pyrolysis products of polypropylene Tatren TF 411. Squalane, 70°C, for identification of the peaks, see Table II.

and dienes are also present, *e.g.* 2,4-dimethyl-1-pentene, 4-methyl-1-heptene, 2-methyl-1,4-hexadiene, *etc.* Some higher fragments cannot be unambiguously identified.

The products of thermal degradation of polystyrenes were analyzed on the two capillary columns. Squalane is more useful for identification as a large quantity of precisely measured retention indices have been published for this phase; it yields, however, a poorer resolution for aromatic hydrocarbons than OV-17.

Krasten 127 is a standard polystyrene to which 5–6% mineral oil is added during manufacture (similarly to Krasten 336). Consequently, decomposition produces

TABLE III

Products of the thermal decomposition of polystyrenes. Pyrolysis temperature 510°C, squalane, 70°C

Peak	<i>I</i>	Krasten 336 X, %	Krasten 127 X, %	Kostil SAN X, %	Product
1	205	2.5	2.4	—	C <sub>1</sub> , C <sub>2</sub>
2	320	2.2	2.0	3.3	C <sub>3</sub>
3	379.5	—	1.2	—	1-butene
4	410.5	4.2	—	0.5	butadienes
5	449.9	1.2	0.9	0.5	3-methyl-1-butene
6	479.3	2.5	2.0	—	1-pentene
7	500	1.2	1.2	0.4	pentane
8	521.5	—	—	6.4	acrylonitrile
9	556.3	0.6	0.6	1.5	2-methyl-3-pentene
10	582.3	0.5	1.0	0.6	1-hexene, 2-methyl- -1-pentene
11	625.6	—	—	0.6	2,3-dimethyl-2-butene, 3,3-dimethyl-1-pentene
12	642.0	1.7	2.8	1.7	benzene
13	654.0	0.5	—	—	4-methyl-1-hexene
14	679.9	0.2	0.2	0.3	1,1,2-trichloroethane
15	749.3	3.1	3.4	3.0	toluene
16	776.0	—	—	0.4	—
17	817.3	0.4	—	—	vinylcyclohexene
18	838.9	0.6	0.7	0.2	ethylbenzene
19	875.8	73.5	79.1	78.6	styrene
20	899.9	0.4	0.5	0.4	isopropylbenzene
21	907.9	0.8	0.5	0.6	C <sub>9</sub> H <sub>16</sub>
22	915.1	0.7	0.5	0.4	allylbenzene
23	926.6	0.2	0.2	0.1	propylbenzene
24	953.6	1.0	0.5	0.5	α-methylstyrene



both styrene monomers and characteristic hydrocarbons as well as large amounts of saturated and unsaturated lower hydrocarbons (Table III).

Krasten 336 is a tough polystyrene to which polybutadiene is added. It is apparent from Table III that the degradation products contain both butadiene and its dimer, vinylcyclohexene.

The polystyrene Kostil SAN is manufactured with addition of acrylonitrile. Plates and granules yielded almost identical spectra for their degradation products. The acrylonitrile monomer was freed by pyrolysis and constituted ~6.5% of the volatile degradation products.

The combination of capillary gas chromatography with pyrolysis has many advantages. In addition to the high resolution of capillary columns, they can be used to measure retention data with great precision. These advantages can be useful in the separation and identification of complicated mixtures of degradation products.

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Translated by M. Štulíková.