

GC-MS OF POLYETHYLENE AND POLYPROPYLENE THERMAL CRACKING PRODUCTS

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Abstract

Low-density polyethylene and polypropylene were thermally decomposed individually in a batch reactor at 450°C as a recycling route from the aspect of the production of petrochemical feedstock. The resulting transformation liquid products were analysed by high resolution gas chromatographic-mass spectrometric analysis. More detailed separation of polyalkenes splitting compounds was achieved using high resolution GC (efficiencies up to 490 000 plates) than before. The GC-MS as well as the dependence of homomorphy factors and isopropyl group increments on the number of carbon atoms of alk-1-enes, alk-2-enes, alka- α,ω -dienes and alkanes were used for identification of separated analytes.

Thermal cracking of LDPE products in the range C₅-C₂₃ were characterized by quintets of peaks in the chromatogram which were assigned to *n*-alkanes, alk-1-enes, (*E*)-alk-2-enes, (*Z*)-alk-2-enes and alka- α,ω -dienes with average quantitative ratio 1 : 1.2 : 0.07 : 0.05 : 0.08. In fraction up to *n*-C₈ 140 GC peaks were separated and identified, including around 30 acyclic octenes.

In contrast to the polyethylene thermal cracking which yields products with straight-chain hydrocarbon structure, polypropylene cracking is characterized by the formation of compounds with branched and high prevailingly unsaturated hydrocarbon structure. The pretention of this analytical problem lies in stereoisomerism and corresponding multicomponentity of branched alkenes, alkadienes and alkanes in a broad range of carbon atoms number as main decomposition products of polypropylene. In the liquid fraction up to *n*-C₈ 84 peaks including around 40 acyclic octenes were identified. Other 149 GC peaks were analysed in the C₉-C₂₅ fraction with quantitative ratio of alkane : alkene : alkadiene equal to 1 : 17 : 4. High resolution GC allowed more detailed and more reliable analysis of multicomponent polyalkenes cracking products.

Key words: High resolution gas chromatographic-mass spectrometric analysis. Polyethylene and polypropylene thermal decomposition products.

1. Introduction

In general, a detailed and reliable analysis of chemical composition of a reaction mixture is an essential assumption for characterization of a chemical reaction. Such an analysis becomes more demanding as the complexity of reaction products increases. Hydrocarbons as products of thermal cracking of polyalkenes represent such complex mixtures where several structural types and their isomers may be present in the reaction mixtures. This poses a challenge for their separation as well as identification. Despite applying moderate efficient capillary gas chromatography (GC) only partial separation of product compounds is achieved due to multicomponentity and close physicochemical properties of analytes. The identification of separated analytes is usually a most difficult step of GC analysis. The problems of identification of gas chromatographic separated analytes are related to the absence of reference materials, lack of published retention data as well as their insufficient reproducibility, insufficient precision of structure-retention relationships, and retention calculation

methods, and with the limitation of hyphenated chromatographic-spectrometric techniques (GC-MSD-FTIRD) as well^[1].

The product distribution of thermal decomposition of polyalkenes has been studied by several authors. Gas chromatographic analysis with mass spectrometric detection showed that polyethylene (PE) degradation products display distinct gas chromatographic patterns of a series triplets composed of the aliphatic hydrocarbons having the same carbon atom number in a broad range of carbon atoms eluted on the apolar stationary phase in the order alka- α,ω -diene, alk-1-ene and *n*-alkane^[2]. Other authors stated that the thermal decomposition of high-density polyethylene (HDPE) yielded characteristic quartets of GC peaks in the chromatogram which were assigned to *n*-alkanes, alk-1-enes, alk-*x*-enes (alkenes with internal double bond), and alka- α,ω -dienes in the range C₄-C₂₂^[3,4]. Predel and Kaminsky^[4] identified alk-*x*-enes in PE degradation product as alk-2-enes. The evolution of semivolatile compounds and toxic by-products in the pyrolysis of polyethylene has been studied from 600 to 900°C and yields of around 150 semivolatile compounds were determined^[5].

Thermal cracking of polypropylene (PP) in comparison with polyethylene gives different distribution components because of different splitting mechanisms of starting polyalkenes^[6,7]. In PP decomposition product the branched isomers are formed due to the branched structure. Marin et al.^[8] determined about 50 compounds up to C₁₁, while 2,4-dimethylhept-1-ene was the most abundant compound. In higher boiling part of PP degradation product the presence of different stereoisomers in polypropylene degradation product was explained and analytically characterized by Jakab et al.^[7]. Trimer 2,4-dimethylhept-1-ene was the main product of polypropylene splitting. Tetramer, pentamer, hexamer and heptamer, i.e. oligomeric alk-1-enes with carbon number $3n$ (C₁₂, C₁₅, C₁₈, C₂₁) where *n* is the number of monomeric units, were other significant splitting compounds. Also the presence of alk-1-enes with carbon number of $3n+1$ (C₁₀, C₁₃, C₁₆, C₁₉), alk-2-enes with carbon number $3n+2$ (C₁₁) and $3n$ (C₉, C₁₂), alkanes with carbon number $3n+2$ (C₁₁, C₁₄, C₁₇), and alka- α,ω -dienes $3n+1$ in a broad range of carbon atom numbers (C₁₀, C₁₃, C₁₆, C₁₉, C₂₂) was ascertained.

Based on the analysis of oils and waxes from low-density polyethylene (LDPE) thermal decomposition at 500°C to 700°C, Williams and Williams^[2] came to the conclusion that the wax was a very pure aliphatic material, with no aromatics and the oils produced up to 550°C also contained no aromatic hydrocarbons or polycyclic aromatic hydrocarbons. Oil/wax products from polyethylene cracking are composed predominantly from straight-chain alkanes and alk-1-enes in the range of carbon atoms from C₈ to C₅₇. The products formed during PP cracking are mostly a complex mixture of branched alkenes and alkanes^[9,10]. Such composition of oil/waxes from cracking of PE or PP at mild temperatures seems to be favourable, because these mixtures may be used as co-feed for many downstream processing units. They may be fed to a steam cracker, to produce reusable alkenes^[11,12] or fed to a catalytic cracker to produce gasoline or upgraded in a hydrocracker^[11]. The content of alkanes, alkenes, alkadienes, and aromatics determines the character of further chemical recycling of cracking products from waste polyalkenes.

In previous works, the capillary gas chromatographic separation systems with moderate high separation efficiency were used for analytical separation of polyalkenes degradation products. The capillary columns (length 25 or 30 m and 250 μm I.D.) coated with a non-polar dimethylsilicone stationary phase were used regularly for separation, and maximum length was 60 m and 250 μm I.D.^[13,14]. The aim of this work was to demonstrate the effect of using the more efficient gas chromatographic separation system for separation, identification and quantification of LDPE and PP thermal cracking products for obtaining more detailed and reliable results on the liquid product composition. The results of the composition of gases from thermal degradation of LDPE and PP were presented in our previous work^[12].

2. Experimental

2.1. Material of LDPE and PP plastics

The polyalkenes: low-density polyethylene ($\rho = 919 \text{ kg}\cdot\text{m}^{-3}$, $\overline{M}_n = 22.000$, $\overline{M}_w = 292.000$), and polypropylene ($\rho = 903 \text{ kg}\cdot\text{m}^{-3}$, $\overline{M}_n = 65.000$, $\overline{M}_w = 200.000$) were obtained from Slovnaft, Inc. (Bratislava, Slovak Republic) and are virgin plastics. The diameter of pellets ranged from 3.5 to 4.5 mm and 3.3 to 4.0 mm for LDPE and PP, respectively.

2.2. Preparation of liquid products from the thermal cracking of polyalkenes

In order to prepare smaller molecules (oils and waxes) better soluble in liquid hydrocarbon fractions we chose thermal cracking of LDPE and PP in a nitrogen atmosphere in a batch reactor at

450°C^[12]. Both polyalkenes were thermally decomposed separately in a stainless-steel batch reactor, which was described in detail in our previous paper^[12]. We fed the reactor with 17 g of LDPE or PP and closed it. To obtain only low heat gradients in the reactor, we gradually heated the polymer with precisely programmed rate of heating. The final temperature of 450°C in the reactor was reached after 45 minutes. This level of temperature in the reactor was maintained for another 35 minutes to allow the release of the maximum amount of decomposing products from the reactor. This construction enables the stirring of the molten polymer by bubbles of flowing nitrogen, which can also help to lower temperature gradients in the melting. The nitrogen was fed into the apparatus as a purge gas, first to prevent the presence of air in the reactor, and second to remove gaseous and condensable products formed during thermal decomposition. The oil/wax fraction was then collected in the separator.

Both LDPE and PP polyalkenes produced a hydrocarbon gas, a light yellow oil/wax fraction and little solid residue. The LDPE yielded a semi-solid oil/wax fraction collected in the separator in the amount of 80 mass % and a dark brown waxy solid residue (5 mass %) on the bottom of the batch reactor. The oil/wax fraction that originated from PP decomposition was less viscous than the one from LDPE and was formed in the amount of 85 mass %. A lower amount of solid residue 0.9 mass % was formed from PP than from LDPE. The oil/wax products were subsequently separated into liquid and solid fractions by fractional distillations under atmospheric and reduced pressure (1.6 kPa) in nitrogen atmosphere. The distillation range of liquids from atmospheric distillation was from 40 to 180°C (PE 1, PP 1) and the final boiling point of liquids from distillation under reduced pressure (PE 2, PP 2) was approximately 325°C. In regard to the initial polyalkene, the yield of liquid distillates from LDPE represented 51.9 mass % and that from PP represented 59.2 mass %. Thereafter, prepared liquid distillates were analysed by high resolution capillary gas chromatography with mass spectrometric detection.

2.3 GC-MS

The products of polyalkenes thermal cracking were separated by high resolution capillary gas chromatography with efficiency up to 490 000 effective plates using Petrocol DH column 150 m x 250 µm i. d., 1.0 µm film (Supelco, Bellefonte, USA) under isothermal (up to C₈)^[15] and temperature-programmed conditions in the range 40-300°C with gradient 1°C/min. (up to n-C₂₃). GC-MS measurements were performed on a gas chromatograph Agilent Technologies 6890N and 5973 Network mass selective detector. Degradation components were identified by comparing measured and published retention data and by structure-retention correlations of hydrocarbon homologous as well as oligomeric series, and mass spectra were interpreted by matching the results with library spectra.

2.4 FIA and PONA analysis

Obtained polyalkenes cracking liquid fractions were also analysed by hydrocarbon group types using displacement liquid chromatography by fluorescence indicator adsorption method (FIA)^[16] and by O-PONA hydrocarbon types GC analysis^[17].

3. Results and discussion

3.1 GC of polyethylene thermal cracking products

The chromatogram of PE 2 product is given in Fig. 1. It is clear that chromatogram obtained in high efficient column contains two dominant products which are alk-1-enes and *n*-alkanes in the range C₆-C₂₃. Beside these main PE decomposition products the chromatogram is fully occupied by several hundreds small peaks of other compounds including "broad peak of many unresolved compounds" which is characteristic for multicomponent hydrocarbon mixtures.

In previous studies^[3,4] on composition of thermal cracking PE product obtained in moderate efficient column a characteristic quartet of GC peaks was ascertained which were assigned as *n*-alkanes, alk-1-enes, alk-2-enes and alka- α,ω -dienes. From comparison of published chromatograms and those measured in this work follows that the peak of alka- α,ω -dienes obtained in moderate efficient column by high resolution column shows the presence of at least two compounds. Follows that quantitative data of alka- α,ω -dienes measured in common efficient capillary columns are surplus value.

The presence of alk-*x*-enes, resp. alk-2-enes was documented in a polyethylene cracking product separated in common capillary column^[3,4]. More efficient separation in high resolution column (Fig. 1) confirmed that corresponding peaks are (*Z*)-alk-2-enes. In moderate efficient column with high

probability these isomers interfered with other product compounds and quantitative data are also surplus value.

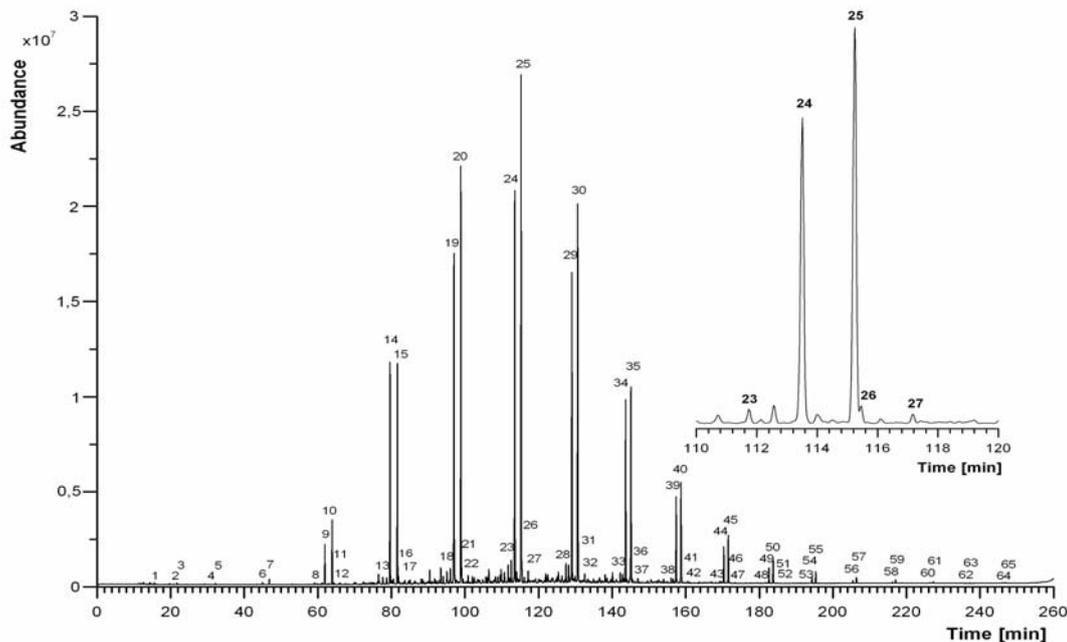


Fig. 1. GC-MS/TIC chromatogram of the separation of polyethylene thermal cracking products (PE 2 fraction). Peak identification as in Table 1

The determined presence of (*Z*)-alk-2-enes was ground to ascertain possible presence of (*E*)-alk-2-enes in the PE decomposition products. The chromatogram in Fig. 2 shows that these (*E*)-alk-2-enes are eluted immediately after *n*-alkanes. This finding suggests that the quantitation of *n*-alkanes is influenced by coelution of (*E*)-alk-2-enes in PE decomposition products analysed in capillary columns of common efficiency.

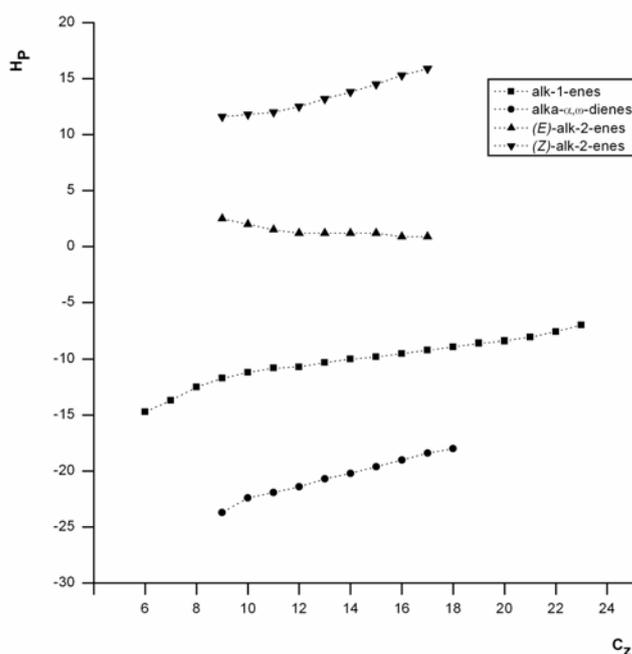


Fig. 2. Dependence of homomorphy factors $H_P = f(C_Z)$ at programmed column temperature for homologues series of alk-1-enes, alka- α,ω -dienes, (*E*)-alk-2-enes and (*Z*)-alk-2-enes from the PE 2 fraction on polydimethylsiloxane

Because of the lack of standard materials and retention data of alka- α,ω -dienes, (*E*)-alk-2-enes and (*Z*)-alk-2-enes with higher carbon atoms number and limitation of mass spectral data for resolution of (*E*)/(*Z*) isomers these analytes were preliminary identified on the basis of homomorphy factors H [1]. The H value is defined as the difference of retention index of the analyte and n -alkane with the same carbon atom number. Under isothermic separation conditions the H values for hydrocarbon homologous series exhibit characteristic moderately non-linear asymptotical decreasing dependence on the number of carbon atoms of homologous. The decrease of H values is apparent up to about six carbon atoms from the beginning of the given homologous structural trait. Based on chromatogram obtained at linear temperature programmed column in Fig. 2, the linear retention indices I_P and temperature programmed H_P values were calculated for alka- α,ω -dienes, alk-1-enes, n -alkanes, (*E*)-alk-2-enes and (*Z*)-alk-2-enes which are given in Table 1. The dependence $H_P = f(C_Z)$ at programmed column temperature is affected also by different retention temperature dependence of analytes. The H_P values increase with increasing number of carbon atoms for (*Z*)-alk-2-enes, alk-1-enes and alka- α,ω -dienes but decrease for (*E*)-alk-2-enes (Fig. 2). The regularities of these dependences allowed preliminary identification of these analytes. Negative temperature coefficients of Kováts retention indices (dI/dT values) of (*E*)-alk-2-enes^[15] affected difficulties in their separation from corresponding n -alkanes with increasing carbon number of n -alkanes and increasing column temperature, respectively. This preliminary identification was confirmed by mass spectrometric detection of separated peaks. On the basis of these results the thermal decomposition of PE can be characterized by quintets of peaks in the chromatogram which were assigned to n -alkanes, alk-1-enes, (*E*)-alk-2-enes, (*Z*)-alk-2-enes and alka- α,ω -dienes. The average weight quantitative ratio for C₆-C₁₄ (area % of TIC) n -alkane: alk-1-ene : (*E*)-alk-2-ene : (*Z*)-alk-2-ene : alka- α,ω -dienes is 1 : 1.2 : 0.07 : 0.05 : 0.08. However, it must be noted that coelution of these with other compounds can not be excluded under high resolution separation system used, what is apparent from quantitative ratio values for some minority analytes given in Table 1.

Table 1 Identification and yield (area % of TIC) of polyethylene thermal cracking product (PE 2 fraction).

Peak No.	Compound	t_R	I_P	% of TIC
1	n-C5	15.62	500.0	0.01
2	1-C6	20.80	585.3	0.01
3	n-C6	21.69	600.0	0.01
4	1-C7	30.71	686.3	0.01
5	n-C7	32.13	700.0	0.02
6	1-C8	44.92	787.5	0.04
7	n-C8	46.75	800.0	0.07
8	α,ω -C9	59.78	876.3	0.03
9	1-C9	61.84	888.3	0.47
10	n-C9	63.83	900.0	0.58
11	(<i>E</i>)-2-C9	64.27	902.5	0.04
12	(<i>Z</i>)-2-C9	65.88	911.6	0.02
11	α,ω -C10	77.56	977.6	0.21
14	1-C10	79.54	988.8	2.84
15	n-C10	81.53	1000.0	2.09
16	(<i>E</i>)-2-C10	81.87	1002.0	0.11
17	(<i>Z</i>)-2-C10	83.57	1011.8	0.07
18	α,ω -C11	95.00	1078.1	0.34
19	1-C11	96.90	1089.2	5.05
20	n-C11	98.77	1100.0	4.52
21	(<i>E</i>)-2-C11	99.01	1101.5	0.21
22	(<i>Z</i>)-2-C11	100.74	1112.0	0.20
23	α,ω -C12	111.65	1178.6	0.53
24	1-C12	113.41	1189.3	6.87
25	n-C12	115.15	1200.0	6.42
26	(<i>E</i>)-2-C12	115.35	1201.2	0.30

Tab. 1 (continued)

27	(Z)-2-C12	117.08	1212.5	0.30
28	$\alpha\omega$ -C13	127.35	1279.3	0.64
29	1-C13	128.96	1289.7	6.33
30	n-C13	130.54	1300.0	6.03
31	(E)-2-C13	130.72	1301.2	
32	(Z)-2-C13	132.44	1313.2	0.35
33	$\alpha\omega$ -C14	142.08	1379.8	0.42
34	1-C14	143.55	1390.0	4.28
35	n-C14	145.00	1400.0	3.57
36	(E)-2-C14	145.17	1401.2	
37	(Z)-2-C14	146.88	1413.8	0.24
38	$\alpha\omega$ -C15	155.95	1480.4	0.31
39	1-C15	157.28	1490.2	2.37
40	n-C15	158.62	1500.0	2.24
41	(E)-2-C15	158.78	1501.2	
42	(Z)-2-C15	160.48	1514.5	0.18
43	$\alpha\omega$ -C16	169.02	1581.0	0.16
44	1-C16	170.24	1590.5	1.24
45	n-C16	171.46	1600.0	1.21
46	(E)-2-C16	171.57	1600.9	
47	(Z)-2-C16	173.32	1615.3	0.07
48	$\alpha\omega$ -C17	181.39	1681.6	0.10
49	1-C17	182.52	1690.8	0.69
50	n-C17	183.64	1700.0	0.80
51	(E)-2-C17	183.74	1700.9	
52	(Z)-2-C17	185.48	1715.9	0.05
53	$\alpha\omega$ -C18	193.15	1782.0	0.07
54	1-C18	194.20	1791.1	0.38
55	n-C18	195.23	1800.0	0.46
56	1-C19	205.35	1891.4	0.20
57	n-C19	206.31	1900.0	0.31
58	1-C20	216.06	1991.6	0.17
59	n-C20	216.95	2000.0	0.19
60	1-C21	226.40	2091.9	0.05
61	n-C21	227.24	2100.0	0.13
62	1-C22	236.48	2192.4	0.26
63	n-C22	237.24	2200.0	0.14
64	1-C23	246.36	2293.0	0.26
65	n-C23	247.05	2300.0	0.16

The use of a capillary column with thick films of stationary phase yields higher retention factors k of lower boiling hydrocarbons and therefore allows to obtain their separation with higher efficiency. In the liquid polyethylene decomposition fraction (PE 1) up to n -octane 140 GC peaks were separated and identified. Acyclic alkenes are prevailing. MS-SIM chromatogram of PE degradation product obtained by detection at molecular ion m/z 112 corresponding to the acyclic octenes (and cycloalkanes) on PDMS column at 30°C is presented in Fig. 3. Out of 93 possible isomeric acyclic octenes, four isomers (3,5-dimethylhex-1-ene, 4,4-dimethylhex-1-ene, 3,4-dimethylhex-1-ene and 4,5-dimethylhex-1-ene) exhibit a zero of M^+ RA (%) value under given MS experimental conditions^[15]. The presence of these isomers by MS-TIC was not confirmed in the PE cracking product. On the basis of published GC-MS data^[15], around 30 acyclic octenes were identified in PE decomposition product (Table 2). The measured indices were in agreement on average by ± 0.1 i.u. with published Kováts retention indices obtained in our previous work^[15].

From these measurements follows that liquid polyethylene cracking product obtained under given cracking conditions yields high and approximately equal amounts of n -alkanes and alk-1-enes; the content of alka- α,ω -dienes, (E)-alk-2-enes and (Z)-alk-2-enes is low. Small amounts of benzene and

toluene were determined from aromatic hydrocarbons in PE 1 product. The sum of aromatic hydrocarbons determined by ASTM D 1319 method ^[16] is 0.9 %, alkanic 28.7 % and alkenic hydrocarbons 70.4 % vol., respectively.

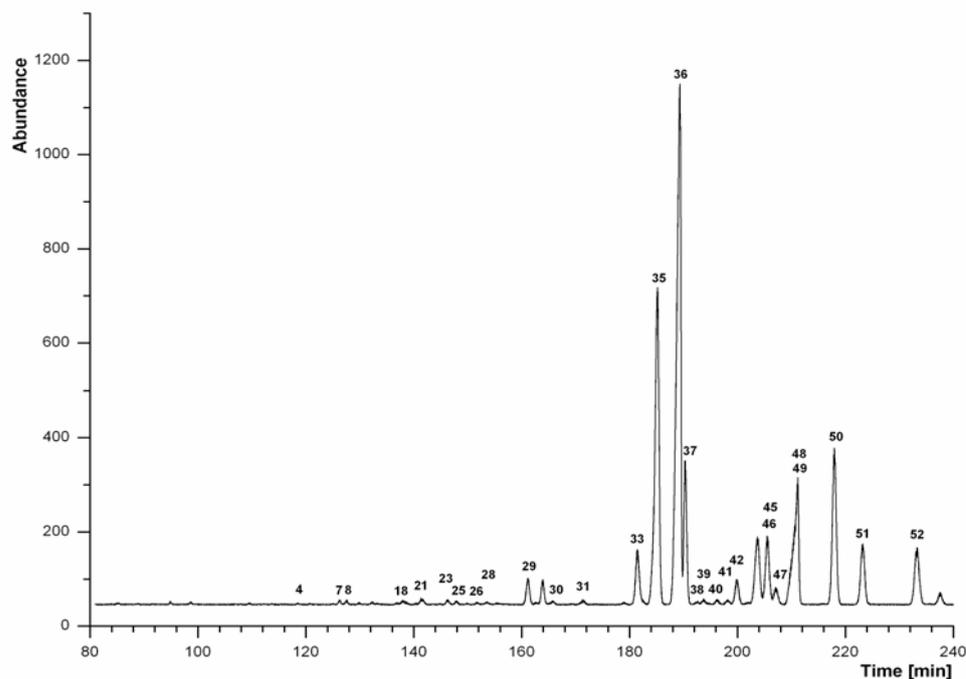


Fig. 3. GC-MS/SIM (m/z 112) chromatogram of the separation of acyclic octenes from the PE 1 fraction. Peak identification as in Table 2

3.2 GC of polypropylene thermal cracking products

In contrast to the thermal polyethylene cracking products with straight-chain hydrocarbon structure, the formation of compounds with branched high prevailing unsaturated hydrocarbons structure is characteristic for polypropylene. It corresponds to the analogous free radical degradation mechanisms and different molecular structure of both polyalkenes ^[18]. Due to the polypropylene branched structure the variety of products is more complex than from PE degradation, and the stereoisomers are formed.

The liquid products of thermal cracking of polypropylene (PP 1 and PP 2) were analysed in same separation system as polyethylene cracking products. In a liquid polypropylene cracking product (PP 1) up to n -octane 84 GC peaks were recorded and identified by means of GC-MS. A part of this chromatogram obtained for acyclic octenes detected at molecular ion m/z 112 under same GC-MS conditions as for PE 1 product is given in Fig. 4. Up to now four acyclic octene isomers (2,4-dimethylhex-1-ene, 2-methylhept-1-ene, 2,3-dimethylhex-2-ene, and 4-methylhept-2-ene without (E)/(Z) configuration) were identified ^[7,8,13], and approximately 40 octene isomers were identified in PP degradation products in this work. The measured retention indices and identification of acyclic octenes from PP 1 degradation product are given in Table 2. The presence of all acyclic pentenes, many acyclic hexenes (most of 2-methylpent-1-ene), heptenes (most of 2,4-dimethylpent-1-ene) and octenes (most of (E)-4-methylhept-2-ene) was found. The most prevailing compound was 4-methylheptane and trimer 2,4-dimethylhept-1-ene up to C_8 and C_9 , respectively.

The chromatogram of PP 2 in Fig. 5 suggests shows more than 400 partially separated GC peaks. Calculated retention indices and identification of some separated compounds are given in Table 3.

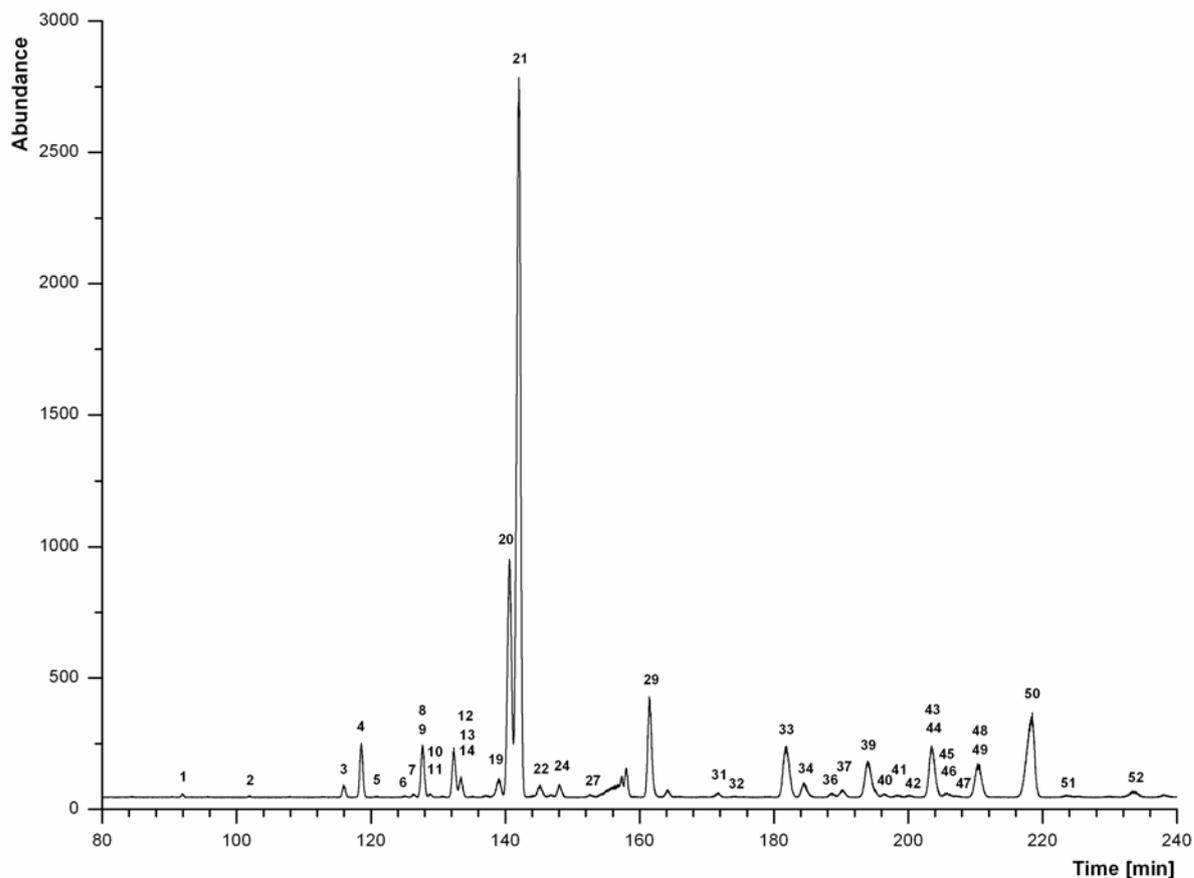


Fig. 4. GC-MS/SIM (m/z 112) chromatogram of the separation of acyclic octenes from the PP 1 fraction. Peak identification as in Table 2

Table 2 Published and measured Kováts retention indices of acyclic octenes from PE and PP cracking products on polydimethylsiloxane at 30 °C (I_{30}^{PDMS})

Peak no.	Octene	I_{30}^{PDMS}		
		Published [15]	Measured PE 1	Measured PP 1
1	2,4,4-Trimethylpent-1-ene	708.6		708.9
2	2-Isopropyl-3-methylbut-1-ene	720.3		720.6
3	(E)-4,4-Dimethylhex-2-ene	735.0		735.1
4	(Z)-2,4-Dimethylhex-3-ene	737.3	737.7	737.6
5	(E)-2,4-Dimethylhex-3-ene	739.6		739.6
6	2,3,3-Trimethylpent-1-ene	743.3		743.4
7	3-Ethylhex-1-ene	744.8	744.7	744.6
8	2,4-Dimethylhex-2-ene	745.7	745.8	745.8
9	2-Ethyl-4-methylpent-1-ene	745.7		
10	(Z)-4,5-Dimethylhex-2-ene	746.5		
11	2,3-Dimethylhex-1-ene	746.7		746.8
12	(Z)-6-Methylhept-3-ene	750.5	750.0	750.6
13	2,4-Dimethylhex-1-ene	750.7		
14	2,5-Dimethylhex-1-ene	750.7		
15	(E)-4-Ethylhex-2-ene	753.5		753.6
16	(Z)-4,4-Dimethylhex-2-ene	753.5		

Table 2 (Continued)

17	2-Isopropylpent-1-ene	753.7		
18	6-Methylhept-1-ene	754.4	754.5	
19	4-Methylhept-1-ene	755.1		755.2
20	(Z)-4-Methylhept-2-ene	756.3		756.4
21	(E)-4-Methylhept-2-ene	757.3	757.2	757.5
22	(E)-6-Methylhept-3-ene	759.8		759.9
23	(Z)-3,5-Dimethylhex-2-ene	761.1	760.9	
24	2,5-Dimethylhex-2-ene	762.0		762.1
25	(E)-3,5-Dimethylhex-2-ene	762.0	762.2	
26	(Z)-3,4-Dimethylhex-2-ene	764.8	764.9	
27	(Z)-2,3-Dimethylhex-3-ene	765.2		765.5
28	(Z)-3,4,4-Trimethylpent-2-ene	766.2	766.2	
29	(E)-6-Methylhept-2-ene	771.5	771.5	771.5
30	(E)-5-Methylhept-2-ene	774.4	774.6	
31	2-Propylpent-1-ene	778.0	778.1	778.3
32	2,3,4-Trimethylpent-2-ene	779.5		779.6
33	2-Methylhept-1-ene	784.3	784.4	784.4
34	3-Ethylhex-3-ene	785.9		785.9
35	2-Ethylhex-1-ene	786.3	786.3	
36	Oct-1-ene	788.3	788.4	788.3
37	(Z)-3-Methylhept-3-ene	789.2	789.5	789.3
38	(E)-3,4-Dimethylhex-3-ene	790.6	790.9	
39	(E)-4-Methylhept-3-ene	791.3	791.4	791.4
40	(E)-3-Ethylhex-2-ene	792.7	792.8	792.7
41	(Z)-3-Ethylhex-2-ene	793.8	793.9	793.8
42	(E)-Oct-4-ene	794.7	794.8	794.7
43	(Z)-3-Methylhept-2-ene	796.7	796.8	796.5
44	(E)-3-Methylhept-3-ene	796.9		
45	(E)-Oct-3-ene	797.7	797.8	797.7
46	(Z)-Oct-3-ene	797.7		
47	(Z)-Oct-4-ene	798.5	798.6	798.3
48	2,3-Dimethylhex-2-ene	800.2		800.0
49	2-Methylhept-2-ene	800.2		
50	(E)-Oct-2-ene	804.0	803.9	803.9
51	(E)-3-Methylhept-2-ene	806.6	806.4	806.3
52	(Z)-Oct-2-ene	811.2	810.9	810.8

For preliminary identification of PP 2 products the dependence of isopropyl group increments of linear retention indices (obtained at linear temperature programmed at column), I_p values, on the number of carbon numbers of oligomeric $3n$ and $3n+1$ alk-1-enes, $3n$ and $3n+2$ alk-2-enes, $n+1$ alka- α,ω -dienes and $3n+2$ alkanes were used; first eluted diastereoisomers which are most abundant compounds were correlated.

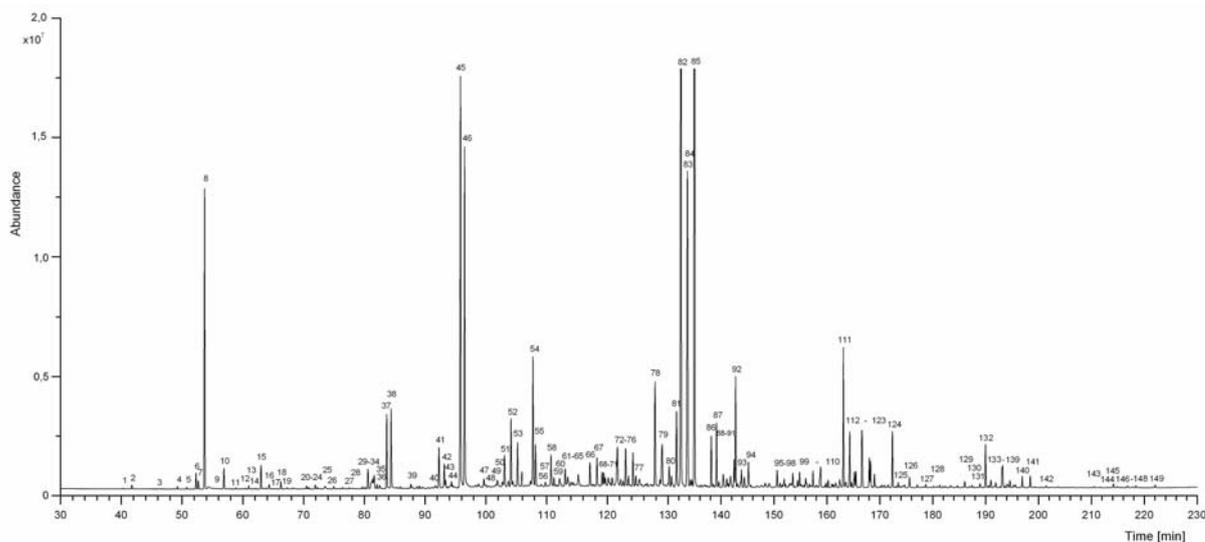


Fig. 5. GC-MS/TIC chromatogram of the separation of polypropylene thermal cracking products (PP 2 fraction). Peak identification as in Table 3

Table 3 Identification and yield (area % of TIC) of polypropylene thermal cracking products (fraction PP 2)

Peak No.	t_R	I_p	Compound	% of TIC
1	40.36	755.9	toluene	0.11
2	41.74	765.3	4-methylheptane	0.05
3	46.09	795.0	C8-diene	0.02
4	49.25	814.3	C9-alkene	0.05
5	50.79	823.2	2,4-dimethylheptane	0.03
6	52.32	832.2	4,6-dimethylhept-2-ene	0.23
7	52.69	834.4	α,α,α -1,3,5-trimethylcyclohexane	0.16
8	53.71	840.3	2,4-dimethylhept-1-ene	2.91
9	55.25	849.3	C9-diene	0.02
10	56.90	859.0	α,α,β -1,3,5-dimethylcyclohexane	0.34
11	58.89	870.7	C9-diene	0.07
12	60.40	879.5	C9-diene	0.01
13	60.99	882.9	C10-alkene	0.05
14	62.21	890.1	1,1,3,5-tetramethylcyclohexane	0.02
15	63.00	894.7	2,4,6-trimethylhept-1-ene	0.25
16	64.33	902.4	C10-diene	0.11
17	65.29	907.8	C10-cyclene	0.03
18	66.28	913.4	2,4,6-trimethylhepta-1,6-diene	0.13
19	67.28	919.1	C10-cyclene	0.06
20	70.47	937.1	C10-alkene	0.04
21	70.79	938.9	C10-alkene	0.03
22	71.94	945.4	C10-alkene	0.04
23	72.32	947.5	C10-alkene	0.02
24	72.86	950.6	C10-diene	0.02
25	73.65	955.0	C10-alkene	0.05
26	74.49	959.8	1,3,5-trimethylbenzene	0.01
27	77.48	976.7	C10-diene	0.05
28	78.20	980.7	C10-diene	0.03
29	79.77	989.6	C10-diene	0.06
30	80.19	992.0	C10-diene	0.05
31	80.60	994.3	4,6-dimethylnon-2-ene	0.22

Table 3 (Continued)

32	81.10	997.1	C11-alkene	0.10
33	81.34	998.4	4,6-dimethylnon-2-ene	0.16
34	81.61	1000.0	4,6-dimethylnon-2-ene	0.16
35	82.09	1002.8	C11-alkene	0.05
36	82.54	1005.4	C11-alkene	0.06
37	83.68	1012.0	4,6-dimethylnonane	0.57
38	84.43	1016.3	4,6-dimethylnonane	0.62
39	87.68	1035.1	C11-alkene	0.04
40	91.73	1058.6	C12-diene	0.06
41	92.28	1061.8	C12-alk-2-ene	0.55
42	93.15	1066.9	4,6,8-trimethylnon-2-ene	0.35
43	93.38	1068.2	C12-alkene	0.07
44	94.36	1073.9	C12-diene	0.09
45	95.82	1082.3	2,4,6-trimethylnon-1-ene	4.18
46	96.51	1086.3	2,4,6-trimethylnon-1-ene	3.19
47	99.68	1105.0	C13-alkene	0.17
48	100.06	1107.3	C13-diene	0.07
49	101.90	1118.5	C13-alkene	0.17
50	102.74	1123.6	C13-diene	0.12
51	103.08	1125.7	C13-diene	0.58
52	104.15	1132.2	2,4,6,8-tetramethylnon-1-ene	0.60
53	105.22	1138.8	C13-diene	0.56
54	107.76	1154.3	2,4,6,8-tetramethylnona-1,8-diene	1.84
55	108.19	1156.9	2,4,6,8-tetramethylnona-1,8-diene	0.61
56	109.12	1162.6	C13-diene	0.14
57	109.80	1166.8	C13-diene	0.14
58	110.74	1172.5	C13-cyclane	0.67
59	111.22	1175.4	C13-alkene	0.09
60	112.13	1181.0	C13-diene	0.11
61	113.06	1186.7	C13-cyklane	0.36
62	113.47	1189.2	C13-alkene	0.19
63	114.02	1192.5	C13-alkene	0.15
64	114.39	1194.8	C13-diene	0.13
65	115.22	1199.8	C13-diene	0.25
66	117.15	1212.4	C13-cyclane	0.47
67	118.29	1219.8	4,6,8-trimethylundec-2-ene	0.38
68	119.15	1225.3	C14-diene	0.28
69	119.44	1227.2	C14-alkene	0.16
70	119.66	1228.7	C14-alkene	0.15
71	120.16	1231.9	C14-alkene	0.13
72	121.66	1241.6	4,6,8-trimethylundecane	0.65
73	122.22	1245.3	C14-alkene	0.12
74	123.02	1250.5	4,6,8-trimethylundecane	0.34
75	123.49	1253.6	C14-diene	0.16
76	124.22	1258.3	4,6,8-trimethylundecane	0.30
77	124.68	1261.3	C14-diene	0.17
78	127.84	1281.8	C15-alkene	1.58
79	129.03	1289.5	4,6,8,10-tetramethylundec-2-ene	0.53
80	130.18	1297.0	C15-alkene	0.52
81	131.59	1306.6	C15-alkene	1.37
82	132.43	1312.4	2,4,6,8-tetramethylundec-1-ene	15.71
83	133.65	1320.8	2,4,6,8-tetramethylundec-1-ene	6.37
84	134.22	1324.8	C16-diene	0.25
85	134.98	1330.1	2,4,6,8-tetramethylundec-1-ene	12.44

Table 3 (Continued)

86	138.15	1352.0	C16-diene	1.19
87	139.16	1358.9	2,4,6,8,10-pentamethylundec-1-ene	0.82
88	139.60	1362.0	C16-diene	0.19
89	140.41	1367.6	C16-diene	0.40
90	141.09	1372.3	C16-alkene + C16-diene	0.19
91	141.79	1377.1	C16-diene	0.29
92	142.76	1383.8	2,4,6,8,10-pentamethylundeca-1,10-diene	2.03
93	143.86	1391.4	C16-diene	0.34
94	145.19	1400.7	C16-diene	0.47
95	150.59	1440.4	4,6,8,10-tetramethyltridec-2-ene	0.32
96	151.93	1450.2	C17-alkene	0.15
97	153.26	1460.0	C17-alkene	0.09
98	153.57	1462.2	4,6,8,10-tetramethyltridecane	0.20
99	154.46	1468.8	C17 -alkene	0.17
100	154.84	1471.6	4,6,8,10-tetramethyltridecane	0.24
101	156.01	1480.2	4,6,8,10-tetramethyltridecane	0.13
102	157.38	1490.3	4,6,8,10-tetramethyltridecane	0.22
103	157.90	1494.0	2,4bis(1,1-dimethyletyl)fenol	0.10
104	158.81	1500.8	C17-alkane + C18-alkene	0.47
105	159.86	1508.9	4,6,8,10,12-pentamethyltridec-2ene	0.11
106	160.25	1512.0	C18-diene	0.19
107	160.95	1517.4	2,5-bis(1,1-dimethyletyl)phenol	0.13
108	161.26	1519.9	C18-alkene	0.08
109	161.69	1523.2	C18-alkene	0.18
110	162.41	1528.8	C18-alkene	0.25
111	163.12	1534.3	2,4,6,8,10-pentamethyltridec-1-ene	2.08
112	163.63	1538.3	C19-diene	0.18
113	164.33	1543.7	2,4,6,8,10-pentamethyltridec-1-ene	0.95
114	164.71	1546.7	C18-alkene	0.15
115	165.19	1550.4	C18-alkene	0.25
116	165.47	1552.6	C18-alkene	0.30
117	166.09	1557.4	C18-alkene	0.03
118	166.63	1561.6	2,4,6,8,10-pentamethyltridec-1-ene	1.26
119	168.01	1572.4	2,4,6,8,10-pentamethyltridec-1-ene	0.45
120	168.25	1574.2	C19-diene	0.71
121	168.99	1580.0	2,4,6,8,10,12-hexamethyltridec-1-ene +	0.22
122	170.39	1590.9	C19-diene	0.09
123	171.56	1599.9	C19-diene	0.10
124	172.39	1606.8	2,4,6,8,10,12-hexamethyltrideca-1,12-diene	1.23
125	173.49	1615.8	C19-diene	0.13
126	175.62	1633.3	C19-diene	0.29
127	178.68	1658.5	4,6,8,10,12-pentamethylpentadec-2-ene	0.09
128	181.34	1680.3	4,6,8,10,12-pentamethylpentadecane	0.08
129	186.06	1720.1	C21-alkene	0.20
130	186.93	1727.6	4,6,8,10,12,14-hexamethylpentadec-2-ene	0.04
131	188.95	1745.0	C21-alkene	0.16
132	189.99	1754.0	2,4,6,8,10,12-hexamethylpentadec-1-ene	0.92
133	190.60	1759.2	C21-diene	0.09
134	191.01	1762.8	C21-alkene	0.21
135	191.93	1770.7	C21-alkene	0.13
136	193.21	1781.8	C21-alkene	0.46
137	193.67	1785.7	C21-alkene	0.07
138	194.62	1793.9	C22-diene	0.28
139	195.27	1799.5	C22-alk-1-ene	0.09

Table 3 (Continued)

140	196.92	1814.4	C21-alkene +	0.29
141	198.44	1828.1	2,4,6,8,10,12,14-heptamethylpentadeca-1,14-diene	0.40
142	201.45	1855.3	C22-diene	0.10
143	210.49	1938.5	C24-alkene	0.07
144	212.99	1962.0	C24-alkene	0.04
145	214.16	1973.0	2,4,6,8,10,12,14-heptamethylheptadec-1-ene	0.18
146	214.74	1978.5	C25-diene + C24-alkene	0.05
147	216.84	1998.3	C24-alkene	0.09
148	218.38	2013.3	C25-diene	0.12
149	222.02	2048.7	2,4,6,8,10,12,14,16-octamethylhepta-1,16-diene	0.14

The regularities of these dependences are demonstrated in Fig. 6, and corresponding identification was confirmed by mass spectrometry.

The following was found in the PP 2 product:

- C₉, C₁₂, C₁₅, C₁₈, C₂₁ and C₂₄ 3*n* alk-1-enes, the most abundant were C₁₅ diastereoisomers of 2,4,6,8-tetramethylundec-1-ene,
- C₁₀, C₁₃, C₁₆, C₁₉ and C₂₂ 3*n*+1 alk-1-enes, the most abundant were C₁₆ diastereoisomers of 2,4,6,8-pentamethylundec-1-ene,
- C₉, C₁₂, C₁₅, C₁₈, and C₂₁ 3*n* alk-2-enes, the most abundant were C₁₅ stereoisomers of 4,6,8,10-tetramethylundec-2-ene,
- C₁₁, C₁₄, and C₁₇ 3*n*+2 alk-2-enes, the most abundant were C₁₄ stereoisomers of 4,6,8-trimethylundec-2-ene,
- C₁₀, C₁₃, C₁₆, C₁₉, C₂₂ and C₂₅ 3*n*+1 alka- α,ω -dienes, the most abundant were C₁₆ diastereoisomers of 2,4,6,8,10-pentamethylundeca-1,10-diene,
- C₈, C₁₁, C₁₄, C₁₇ and C₂₀ 3*n*+2 alkanes, the most abundant were C₁₄ diastereoisomers of 4,6,8-trimethylundecane.

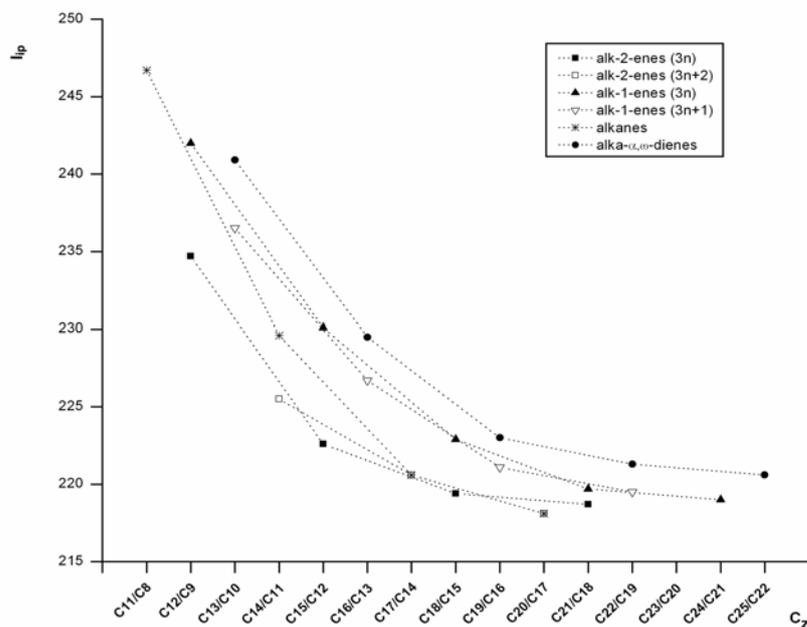


Fig. 6. Dependence of isopropyl group increments of linear retention indices I_{ip} on the number of carbon atoms of alk-2-enes, alk-1-enes, alkanes and alka- α,ω -dienes from the PP 2 fraction on polydimethylsiloxane

The 149 GC peaks were analysed in the C₉-C₂₅ range. Overall quantified area of gas chromatographic peaks corresponds of 83.4 % to the identified compounds. On the basis of obtained chromatogram the calculated ratio of alkane : alkene : alkadiene in thermal cracking product of polypropylene is 1 : 17 : 4 (area % of TIC). Using an ASTM D 1319 method 5.5 % of alkanic, 93.3 % alkenic and 1.2 % vol. of aromatic hydrocarbons were determined.

The pretension of this analytical problem lies in stereoisomerism thus in the multicomponentity of branched alkenes, alkadienes and alkanes as main decomposition products of polypropylene. In the case of alk-1-enes which are the most abundant components, there are two possible diastereoisomers for 2,4,6-trimethylnon-1-ene, which are base-line separated also in column with moderate efficiency. The number of possible diastereoisomers increases with higher analysed alkene oligomers, e.g. there are four possible diastereoisomers for 2,4,6,8-tetramethylundec-1-ene, and eight possible diastereoisomers for analysed 2,4,6,8,10-pentamethyltridec-1-ene. For other hydrocarbon groups, e.g. for 4,6,8,10-tetramethyltridecane, there are six possible diastereoisomers, and for 2,4,6,8,10-pentamethylundeca-1,10-diene, there are three possible diastereoisomers. In the case of alk-2-enes the situation is more complex because of addition of asserting (*E*)/(*Z*) isomerism. Higher stereoisomers are eluted in a relative broad retention range, and the possibilities of separation interference of stereoisomeric alkenes, alkadienes and alkanes as well as other hydrocarbon types as PP cracking product components increases with an increasing number of carbon atoms

4. Conclusions

The advantages of the use of high resolution GC in analysis of polyalkenes degradation products include better separation of multicomponent product mixtures, more characteristic measured mass spectra, the decrease of base-line increase of unresolved GC peaks that leads to the more reliable identification and to more precise quantitative results. Based on using high resolution GC, more compounds, mainly isomeric acyclic alkenes, were ascertained in polyethylene and polypropylene degradation products when compared with those described in earlier literature reports. More detailed and reliable qualitative and quantitative results poses presumption for more detailed explanation of reaction mechanism and better optimization of reaction process for obtaining wishing products.

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