
IR-SPECTROSCOPIC STUDY OF THE CONDENSATION PRODUCTS OF HEAT-DEGRADATION OF POLYETHYLENE AND POLYPROPYLENE IN INERT ATMOSPHERE

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Received November 3, 1989

Accepted February 21, 1990

Infrared spectra of condensates generated by heating of polyethylene and polypropylene in inert atmosphere for various times at 300, 400, 500 and 600°C were measured. The condensed products were characterized by means of infrared spectra. It was found that IR-spectra are suitable for determining the thermal history of polyethylene and polypropylene degradation.

The mechanism of thermal degradation of macromolecular compounds is of interest both from the point of view of the basic research of polymer reactions, and for purely practical reasons, for example for the preparation of waxy oligomers, effective utilization of plastic waste as secondary raw materials, etc. Thermal degradation can lead to changes in the molecular weight of the polymer either by separation of monomer from the ends of a macromolecule (e.g. polystyrene), or by random splitting of chains with possible generation of new structures.

In most papers¹⁻³ devoted to polyolefin degradation, viscosity measurements are used to indicate which of these processes is occurring in the polymer. Based on an increase in polyethylene viscosity at temperatures around 200°C, Witt and Hogan⁴, and Tanaka et al.⁵ assume that the molecular weight of the polymer increases by long-chain branching. Similar results were obtained by Holmström and Sörvik⁶ using gel permeation chromatography and viscosity measurements of polyethylene degraded at 284 and 335°C in nitrogen.

The structural changes assumed to occur during thermal degradation of polyethylene, as determined indirectly from changes in physical properties (GPC, viscosity), were both qualitatively and quantitatively investigated by Kuroki et al.⁷, who determined by means of IR, ¹H NMR and ¹³C NMR spectroscopy the number of double bonds generated in the macromolecule, as well as long-chain branching for polyethylene thermally degraded at 390°C for 30 to 180 min. Their results indicate that the number of methyl end groups, double bonds (end vinyl, *trans*-vinylene and vinylidene groups) and long-chain branchings per 1 000 carbons increases with

time, while the ratio of these functional groups remains roughly constant. In spite of the importance of these facts calling for more detailed studies, so far nobody has measured the variation with time of thermal degradation of plastics at various temperatures.

The aim of the presented work was to determine by infrared spectroscopy the behaviour and structural changes in linear and branched polyethylene and polypropylene in nitrogen atmosphere, in dependence on the time spent at the selected temperatures.

EXPERIMENTAL

Polymers investigated were the linear polyethylene Liten 5317 (density 961 kg m^{-3}), high pressure branched polyethylene Bralen VA-20-12 (density $915\text{--}918 \text{ kg m}^{-3}$), and polypropylene Mosten 52512 (density 907 kg m^{-3}). The polymers were thermally degraded at 300 and 600°C for one hour, and at 400 and 500°C for 0.5 , 1 , 2 and 4 h.

Thermal degradation of polymers was performed using the apparatus shown in Fig. 1. It consists of an electric oven, in which the temperature is measured with a NiCr-Ni thermocouple connected with an Ahlborn regulator, controlling the temperature to within $\pm 5^\circ\text{C}$. The polymer (5 g) was heated at temperatures below 450°C in a closed stainless steel cylinder and at temperatures above 450°C in a glass vessel provided with a nitrogen inlet port, and an exhaust for the generated gaseous degradation products. The generated vapours from the liquid products were trapped and returned to the reaction zone by an air-cooled condenser, connected with an exhaust for withdrawing the gaseous products. After the given degradation time, the vessel with the polymer was cooled by a stream of air to room temperature within about 5 min . The flow of nitrogen was maintained at $20 \text{ cm}^3 \text{ min}^{-1}$.

Infrared spectra of the starting and degraded polymers in the range $4000\text{--}600 \text{ cm}^{-1}$ were measured using the KBr technique and the Perkin-Elmer 983 G spectrometer, with a resolution of 3 cm^{-1} . For the die with a diameter of 13 mm , the sample weight was 1.5 mg of polymer per 150 mg of KBr.

RESULTS AND DISCUSSION

Liten 5317

The IR spectrum of standard linear polyethylene (Fig. 2, spectrum a) exhibits in the range $2000\text{--}600 \text{ cm}^{-1}$ bands at 719 , 731 and 910 cm^{-1} , a group of weak unresolved bands in the range $1050\text{--}1200 \text{ cm}^{-1}$, 1305 , 1369 , 1383 , 1461 , 1471 cm^{-1} , a broad band at $1550\text{--}1700 \text{ cm}^{-1}$ and a weak band at 1730 cm^{-1} .

The bands at 719 and 731 cm^{-1} are assigned to rocking vibrations of CH_2 groups in the chain^{8,9}. Their mutual ratio indicates the crystallinity degree of polyethylene, as the band at 731 cm^{-1} does not occur in amorphous samples.

The band at 910 cm^{-1} is assigned to the vibration of vinyl end groups^{7-9,11}. The group of weak unresolved bands in the range $1050\text{--}1200 \text{ cm}^{-1}$ is assigned to

mixed twisting-rocking vibrations of methylene groups⁸. The band at 1305 cm^{-1} is assigned to the wagging vibration of the methylene group and it is characteristic of amorphous sequences in chains with GTG^* (G^* is G^+ or G^-) conformation⁹. This band is almost absent in highly crystalline polyethylenes. The bands at 1369 and 1383 cm^{-1} in crystalline samples correspond to the coupling of the symmetrical bending vibration of the methyl group with the wagging vibrations of methylene groups in GTG^* conformation^{8,10}.

The doublet at 1461 and 1471 cm^{-1} corresponds to the scissoring vibration of methylene groups in the chain. The splitting of the methylene group rocking vibration around 720 cm^{-1} and of the methylene group bending vibration around 1470 cm^{-1} can be explained by intermolecular interaction of macromolecules, strongly dependent on crystalline and conformational structure^{8,10}.

The strong band in the range of 1650 cm^{-1} is caused by water absorbed by potassium bromide from air during pellet preparation and the weak band at 1730 cm^{-1} can be assigned to products of polyethylene oxidation⁹.

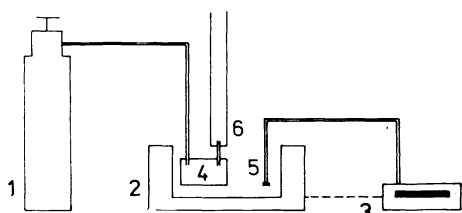


FIG. 1

Apparatus for thermal degradation of polymers: 1 nitrogen reservoir, 2 electric oven, 3 regulator, 4 vessel with polymer, 5 thermocouple, 6 air-cooled condenser

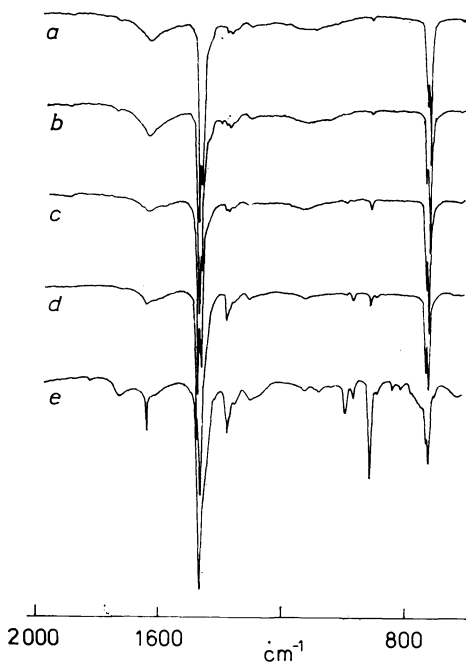


FIG. 2

Infrared spectra of Liten 5317 (*a*) and of its condensed decomposition products after heating for 1 h at *b* 300, *c* 400, *d* 500, and *e* 600°C

After one hour of heat treatment at 300°C the spectrum of polyethylene (*b* in Fig. 2) does not indicate any appreciable chemical change. The decrease in the ratio of the CH₂ rocking bands, together with the increase in the ratio of the methylene scissoring vibration bands (Table I) indicate a decrease in crystallinity caused by rapid cooling of the melt, during which the long chains do not have sufficient time to be arranged in the crystalline structure.

TABLE I

Intensities in band maxima and their ratios used to characterize thermal degradation of linear and branched polyethylene: I_{1378} bending vibration of methylene groups; I_{731} , I_{719} rocking vibrations of methyl groups; I_{1461} , I_{1471} scissoring vibrations of methylene groups; I_{890} vibration of vinylidene groups; I_{910} vibration of vinyl groups

Heating		$I_{1378} \cdot 10^4$	$\frac{I_{731}}{I_{719}}$	$\frac{I_{1461}}{I_{1471}}$	$\frac{I_{890}}{I_{910}}$	$\frac{I_{890}}{I_{1378}}$
°C	h					
Linear polyethylene (Liten 5317)						
—	—	—	0.568	0.778	0	0
300	1	—	0.466	0.753	0	0
400	0.5	110	0.580	0.833	0.079	0.109
	1	118	0.632	0.839	0.084	0.153
	2	185	0.652	0.877	0.137	0.200
	4	405	0.713	1.187	0.363	0.238
500	0.5	526	0.795	1.409	0.343	0.252
	1	546	0.783	1.471	0.377	0.191
	2	577	0.775	1.453	0.481	0.176
	4	678	0.715	1.645	0.471	0.163
600	1	715	0.713	—	0.130	0.315
Branched polyethylene (Bralen VA-20-12)						
—	1	400	0.479	0.928	—	0.091
300	1	431	0.495	0.921	—	0.102
400	0.5	470	0.568	0.903	—	0.071
	1	476	0.624	0.961	1.750	0.110
	2	485	0.628	0.900	1.121	0.178
	4	487	0.651	0.994	0.963	0.257
500	0.5	679	0.777	1.343	0.552	0.290
	1	685	0.775	1.546	0.724	0.245
	2	713	0.750	1.652	0.747	0.215
	4	726	0.693	—	0.522	0.141
600	1	1 590	0	—	0.252	0.435

In spectra of samples degraded at 400°C and above (Fig. 2, spectra *c–e*), new bands appear at 890, 965, 990, 1 378 and 1 640 cm^{-1} , and the intensity of the band at 910 cm^{-1} is enhanced. The bands at 910, 990 and 1 640 cm^{-1} correspond to the vibration of a vinyl end group^{7–9,11}. The band at 965 cm^{-1} corresponds to a *trans*-vinylene group^{8,9}. The band at 890 cm^{-1} is usually assigned either to the vibration of a vinylidene group^{9,11}, or to a vibration corresponding to main chain branching by aliphatic substituents with a number of carbon atoms exceeding six^{7,8}. The band at 1 378 cm^{-1} is assigned to the bending vibration of a CH_3 group⁹.

The time dependence of the changes in IR spectra of Liten 5317 degraded at 400°C indicates that with increasing heating time, a growth in band intensity is observed for the methyl group bending vibration at 1 378 cm^{-1} (Table I), for the vinyl end group vibrations at 910, 990 and 1 640 cm^{-1} , for the band of the *trans*-vinylene group at 965 cm^{-1} , and for the band of the vinylidene group at 890 cm^{-1} . A change in the intensity ratio of the bands of the methylene group vibration at 1 471 and 1 461 cm^{-1} during degradation indicates that in the degraded samples, the population of GT_mG^* conformational structures (m is large), corresponding to the wavenumber 1 461 cm^{-1} (ref.¹⁰) is increased. The gradual growth of the mutual intensity ratio of the CH_2 rocking vibration bands at 731 and 719 cm^{-1} indicates that the crystallinity of the polymer increases even when the samples were obtained by rapid cooling of the melt. Changes in the intensity ratio of the above mentioned bands, together with the growing content of methyl and vinyl end groups indicate that destruction of the polyethylene chain already occurs during heating to 400°C. Thanks to their better mobility, during rapid cooling shorter macromolecules more easily assume the compact crystalline structure.

With increasing time of heating of linear polyethylene at 500°C, only an increase in the intensity of the methyl group band is observed in the spectra (Fig. 3). The intensities of bands corresponding to vinyl, *trans*-vinylene and vinylidene groups after 30 min of heat treatment are higher than after four hours at 400°C. However, at longer duration of degradation at 500°C, the content of double bonds in the product is approximately constant, or it decreases slightly (Table I). The decline in the band ratio of the methylene group rocking vibration in the range of 720 cm^{-1} , together with the declining band ratio of the methylene group scissoring vibration in the range of 1 470 cm^{-1} , indicate a decrease in the content of the crystalline phase in the degraded polymer, and an increase in the population of gauche conformations. This is also confirmed by the band at 1 455 cm^{-1} corresponding to the bending vibration of methylene groups in GT_mG^* conformational structures (m is small)¹⁰, which appears in the spectrum after four hours (spectrum *d* in Fig. 3).

The final product of thermal degradation of Liten 5317 at 600°C has the character of vaseline. The high intensity of the bands of methyl and vinyl group bending vibrations, and of the scissoring vibration of methylene groups in gauche conformations, the missing band of the scissoring vibration of CH_2 groups in the crystalline phase

(1471 cm^{-1}) indicate that the sample predominantly represents an amorphous mixture of oligomers with a large number of methyl and vinyl end groups (cf. spectrum e in Fig. 2).



FIG. 3

Infrared spectra of condensed decomposition products obtained by heating Liten 5317 at 500°C for *a* 0.5, *b* 1, *c* 2, and *d* 4 h

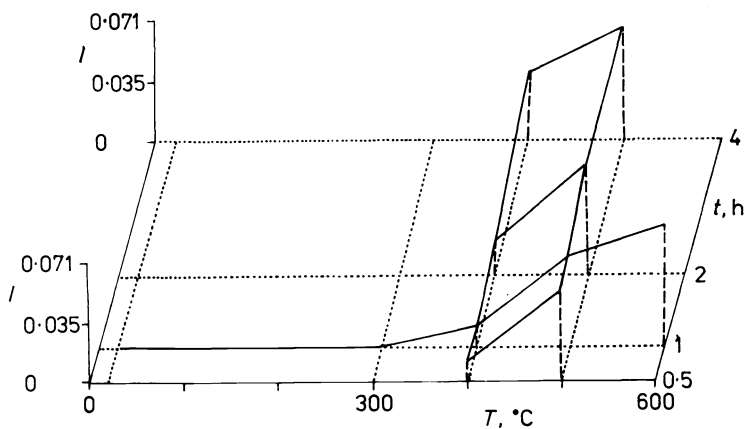


FIG. 4

Dependence of the band intensity of the methyl group bending vibration (I at 1378 cm^{-1}) on temperature (T) and time (t) for linear polyethylene (Liten 5317)

A comparison of IR spectra of polyethylene heated for various times at 300 to 600°C indicates that in samples heated to 400°C, the degree of degradation as characterized by the intensity of the band corresponding to generated methyl end groups, or by mutual band intensity ratios, does not reach the degradation degree of Liten 5317 heated to 500°C (Table I). By comparing mutual band intensity ratios for various samples it is therefore possible to determine both the temperature and the time of polymer heating (Table I). The changes occurring during thermal degradation of Liten 5317 are also clearly reflected in the graph representing the variation of the absorbance intensity of the methyl group band with temperature and time (Fig. 4).

Bralen VA-20-12

The IR spectrum of branched polyethylene (Fig. 5, spectrum *a*) in the range 2 000 to 600 cm^{-1} exhibits bands at 719 cm^{-1} with a shoulder at 730 cm^{-1} , further at 890 cm^{-1} , a group of weak bands in the range 1 050–1 200 cm^{-1} , at 1 305, 1 378, 1 471 cm^{-1} and a weak band at 1 730 cm^{-1} . In view of the presence of aliphatic side chains in the studied sample, the band at 890 cm^{-1} is assigned to the vibration characteristic of long-chain branching in macromolecules^{7,8}, the band at 1 378 cm^{-1} is assigned to the bending vibration of a methyl group^{7,9,10}. The assignment of the other bands is the same as in the spectra of linear polyethylene Liten 5317. The appearance of only a single band of the CH_2 rocking vibration in the range around 720 cm^{-1} , and of a single band of the methylene scissoring vibration around 1 470 cm^{-1} indicates that backbone branching prevents the macromolecules from assuming a compact crystalline structure, so that Bralen VA-20-12 is predominantly amorphous.

After one hour of heating at 300°C, the spectrum of branched polyethylene exhibits no chemical or conformational changes.

The spectra of samples degraded at 400°C and above (Fig. 5, spectra *b–d*) exhibit new bands at 910, 990 and 1 640 cm^{-1} , characteristic of a vinyl end group^{7–9,11}, and a band at 965 cm^{-1} assigned to the vibration of a trans-vinylene group^{8,9}. In analogy to linear polyethylene, also in the case of Bralen VA-20-12 prolonged heating at 400°C leads to a slight intensity increase of the bands assigned to the vinyl end group (910, 990, 1 640 cm^{-1}) and of the band of the methyl group bending vibration (1 378 cm^{-1}). The gradual increase in the intensity of the band of the rocking vibration of CH_2 groups in the crystalline phase^{8,9}, with a wavenumber of 731 cm^{-1} , and the intensity growth of the band of the scissoring vibration of a methylene group in the crystalline phase^{8,9}, with a wavenumber of 1 461 cm^{-1} , leads after four hours of heating to the formation of doublets in the ranges of 720 cm^{-1} and 1 470 cm^{-1} (Fig. 6). Crystalline fractions are present even in standard branched polyethylene, or in the sample after 30 min heat treatment at 400°C, but they are not very conspicuous (spectra *a* in Figs 5 and 6). At 400°C and above, destruction of macromolecules occurs at the tertiary carbon site, and the generated linear chains

can give rise to a crystalline phase. Therefore the band at 890 cm^{-1} can be assigned to the vibration of long-chain branching only to temperatures not exceeding 400°C ; at high temperatures this band corresponds to the vibration of a vinylidene group.

At 500°C the behaviour of branched polyethylene is analogous to that of the linear polyethylene, Liten 5317, i.e. with prolonged heating time the number of CH_3 groups increases and the content of double bonds in the sample decreases. However, the degradation process is more rapid. More rapid degradation at equal temperatures and times is indicated by the higher content of methyl end groups in degraded samples of branched polyethylene, as compared to the linear polymer (Tables I and II), as well as by the band intensities of vinyl end groups ($910, 990, 1\,640\text{ cm}^{-1}$) in the spectra of degraded Liten 5317 and Bralen VA-20-12 (spectrum *d* in Fig. 2, spectrum *c* in Fig. 5). After four hours of treatment at 500°C , Liten 5317 has the character of a wax, while Bralen VA-20-12 has the character of vaseline already after two hours.

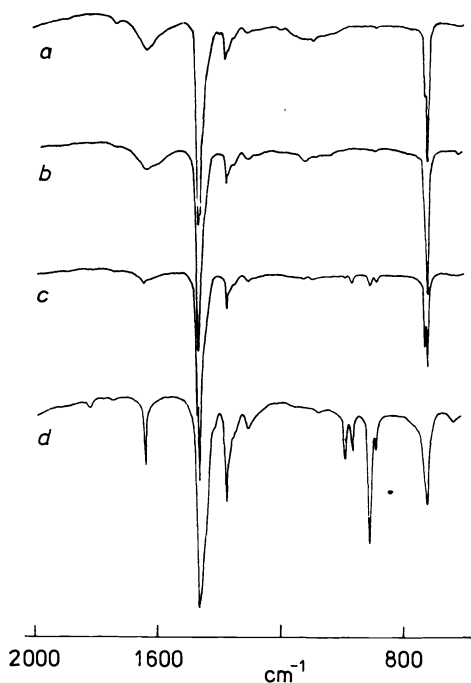


FIG. 5
Infrared spectra of Bralen VA-20-12 (*a*) and of its condensed decomposition products after heating for 1 h at *b* 400, *c* 500, and *d* 600°C

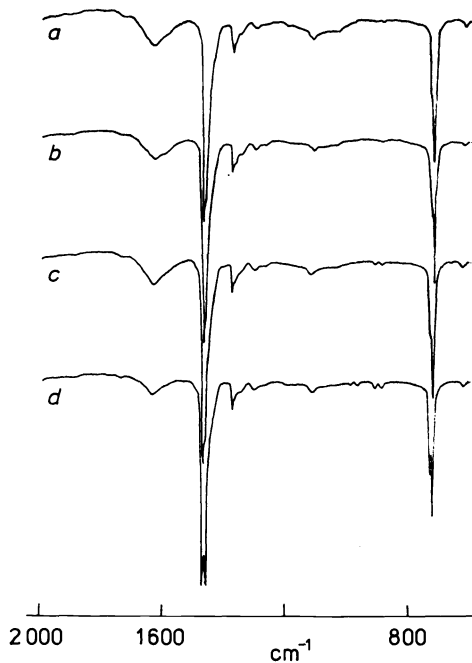


FIG. 6
Infrared spectra of condensed decomposition products obtained by heating Bralen VA-20-12 at 400°C for *a* 0.5, *b* 1, *c* 2, *d* 4 h

The final product of heat degradation of Bralen VA-20-12 at 600°C is a thick oily liquid with an oligomer suspension. Spectrum *e* in Fig. 5 indicates that it contains a large amount of unsaturated bonds.

Similarly as with linear polyethylene, the absorbance intensity of the band at 1378 cm⁻¹ (referred e.g. to 1.5 mg of polyethylene) and the mutual band intensity ratios shown in Table I may be used to determine the thermal history of the sample.

Mosten 52512

According to data published in ref.⁹, the wavenumbers and band assignments of standard Mosten 52512 (Fig. 7 spectrum *a*) correspond to crystalline isotactic polypropylene. The broad band around 1650 cm⁻¹ is caused by water absorbed by potassium bromide from air during pellet preparation, and the weak band around 1740 cm⁻¹ can be assigned to products of polypropylene oxidation.

After one hour of heat treatment at 300°C, the spectrum of polypropylene does not exhibit any change.

The IR spectra of samples heated to 400°C exhibit new bands at 889 and 1648 cm⁻¹, (spectra *b* in Figs 7 and 8), assigned to a vibration of the vinylidene group^{8,9,11}. Their intensity rapidly grows with increasing time of heating (Fig. 8,

TABLE II

Intensities in band maxima and their ratios used to characterize thermal degradation of polypropylene (Mosten 52512): I_{889} vibration of vinylidene group; I_{1166} stretching vibration of the backbone C-C rocking vibration of methyl groups, and wagging vibration of C-H groups; I_{1254} twisting vibration of methylene groups; I_{1378} bending vibration of methyl groups; I_{1043} stretching vibration of the backbone C-C

Heating		$I_{889} \cdot 10^4$	$I_{1166} \cdot 10^4$	$\frac{I_{1254}}{I_{1378}}$	$\frac{I_{1043}}{I_{1378}}$	$\frac{I_{889}}{I_{1378}}$
°C	h					
—	—	0	130	0.895	0.284	—
300	1	0	127	0.950	0.269	—
400	0.5	13	125	0.863	0.246	0.032
	1	56	123	0.598	0.199	0.112
	2	134	106	0.313	0.109	0.197
	4	198	76	0.164	0.055	0.257
500	0.5	177	103	0.311	0.112	0.279
	1	138	68	0.243	0.085	0.268
	2	102	21	0	0	0.707
	4	91	0	0	0	0.714
600	1	88	14	0	0	0.674

Table II), so that after four hours at 400°C it is higher than after 30 min at 500°C (referred to 1.5 mg of polymer in a KBr pellet).

After increasing the temperature to 500°C, further two bands appear (Fig. 7, spectrum c), a weak band at 910 cm^{-1} corresponding to the vibration of a vinyl end group^{7-9,11}, and on the band at 972 cm^{-1} (rocking vibration of a methylene group and a backbone C-C stretching vibration) a shoulder becomes visible at 965 cm^{-1} ; this can be assigned to the vibration of a *trans*-vinylene group^{8,9}. In analogy to the polyethylenes, prolonged treatment at 500°C leads to a decline in the intensity of bands corresponding to double bonds. Simultaneously an intensity drop is also observed for the bands at 1 166 cm^{-1} (backbone C-C stretching vibrations, rocking vibrations of methyl groups, and wagging vibrations of C-H groups) and at 1 458 cm^{-1} (methyl group bending vibrations), and an intensity increase for the bands at 1 150 cm^{-1} (backbone C-C stretching vibrations and bending vibrations of C-H groups) and at 1 450 cm^{-1} (methyl group bending vibrations). This indicates a gradual decline in the crystallinity of these samples⁹ (see Table II).

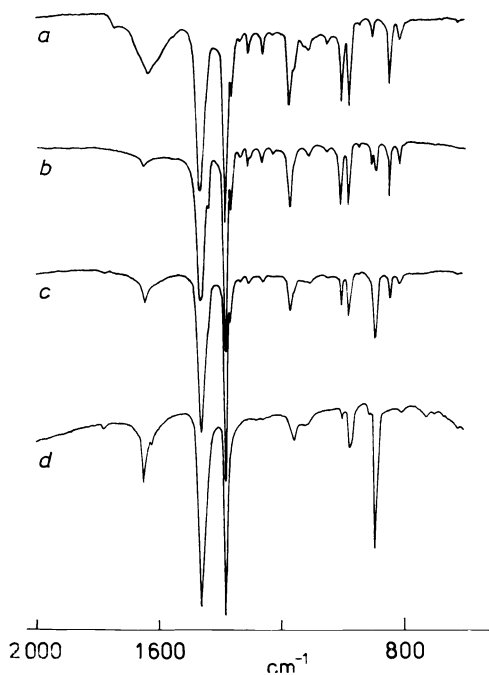


FIG. 7
Infrared spectra of Mosten 52512 (a) and of its condensed decomposition products after heating for 1 h at b 400, c 500, d 600°C

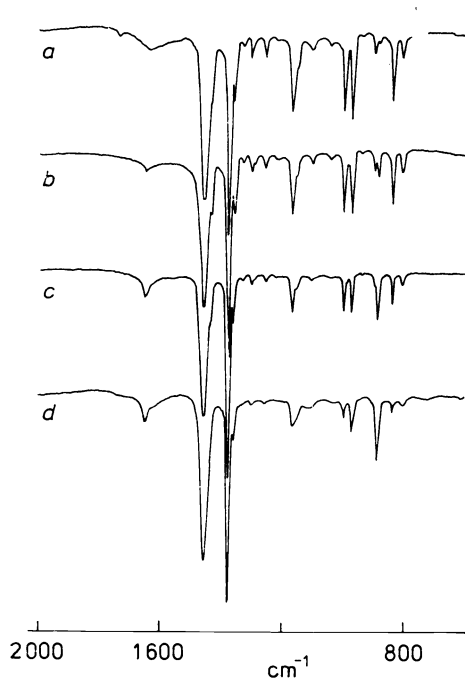


FIG. 8
Infrared spectra of condensed decomposition products obtained by heating Mosten 52512 at 100°C for a 0.5, b 1, c 2, d 4 h

At 600°C, complete destruction of polymer chains takes place. The degradation product is a liquid mixture of unsaturated low-molecular hydrocarbons. In spectrum (d in Fig. 7) bands characteristic of polypropylene do not appear.

The decrease in the mutual intensity ratio of the bands at 1 254 cm^{-1} (twisting vibration of CH_2 groups) and 1 378 cm^{-1} (bending vibration of CH_3 groups), the decreasing intensity of the band of the backbone C–C stretching vibration (1 043 cm^{-1}) with respect to that of the band of the methyl group bending vibration (1 378 cm^{-1}), as well as the increasing band intensity ratio of the vinylidene (889 cm^{-1}) and methyl group bending vibrations (1 378 cm^{-1}) indicates (Table II) that degradation does not involve separation of methyl groups from the macromolecule, but that it proceeds by way of chain splitting with the formation of double bonds. From the mutual band intensity ratios shown in Table II, the thermal history of the sample can be safely determined, i.e. the temperature and duration of the degradation process can be found by comparing mutual band intensity ratios of the unknown sample with the corresponding band intensity ratios in the table.

A comparison of the experimental data indicates that the thermal stability of the polymers decreases in inverse proportion to the number of tertiary carbons in the macromolecule. Linear polyethylene is the most stable, while polypropylene exhibits the lowest heat resistance. In the branched polyethylene Bralen VA-20-12, easier splitting at tertiary carbon atoms at elevated temperatures leads to the formation of linear chains. For polymers with known infrared spectra in the undegraded state, the temperature and duration of heating to which the sample had been exposed can be determined from the band intensity of the methylene group bending vibration, and from the intensity ratios of the band pairs given in Tables I and II.

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Translated by D. Doskočilová.