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Study of the Thermal Degradation of Polyethylene

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Using infrared spectroscopy, we have investigated the changes occurring in the structure of polyethylene (PE) during its thermal degradation. Studying the thermal degradation of PE, Oakes and Richards (^1) suggested that depolymerization of PE is a chain reaction.

The data of Oakes and Richards indicated some preference for rupture of the polymer chain near branching points at the initial stages of degradation and preferential rupture of the unbranched chain at subsequent stages.

Table 1

Effect of thermal degradation on the content of double bonds in PE

PE type	Pyrolysis conditions: temperature, °C	Pyrolysis conditions: duration, h	Double bonds per 1000 C	Saturation distribution, %: RCH=CHR, trans	Saturation distribution, %: $RCH=CH_2$	Saturation distribution, %: $R_2C=CH_2$
PEHD	Initial		0.9	21	18	61
PEHD	360	4	4.6	32	40	28
PEHD	360	6	5.3	36.5	36.5	27
PEHD	415	3	17.3	50	27	23
PELD	Initial		0.8	25	57	17
PELD	360	4	2.5	34	58	8
PELD	360	6	4.0	41	48	11
PELD	415	3	19.8	50	30	20
RPE	Initial		0.5	38	20	42
RPE	360	4	3.1	30	49	21

Oakes and Richards carried out experiments with high-pressure PE in the range from 315 to 360°. We investigated the thermal degradation of three types of PE with different degrees of branching over a broader temperature range from 300 to 415°. Samples of high- and low-pressure PE (PEHD and PELD), as well as PE obtained by radiation polymerization (RPE), were subjected to pyrolysis in sealed glass ampoules in which a vacuum of 10^{-4} mm Hg had first been created. The furnace temperature was regulated by a PSR-1 potentiometer with an accuracy of ±5°. To measure the infrared spectra, PE samples were pressed into metal frames with a thickness from 0.25 to 0.5 mm. The IR spectrum of the liquid obtained during pyrolysis of PE at 415° was measured in a cuvette made of NaCl disks, with a layer thickness of 0.04 mm, on an H-800 double-beam infrared spectrophotometer. The degree of branching of the initial PEHD and RPE was determined by the method and calculation formulas given in papers (^2, ^3).

The number of methyl groups per 1000 carbon atoms in the chain, N_{CH3}, calculated in this way is 21.9 for PEHD and 5.5 for RPE. For PELD, according to Smith' s data (^4), this value is 3. The number of double bonds in the samples studied was determined from absorption bands in the IR spectra at 966, 910, and 888 cm^{-1}, corresponding to out-of-plane deformation vibrations of CH bonds in the groups RCH=CHR-trans,

$\mathrm{RCH{=}CH_2}$ and $\mathrm{R_2C{=}CH_2}$. The extinction coefficients for these bands were taken from work (^{2}).

As can be seen from the data in Table 1, during pyrolysis of PE at 360° the increase in unsaturation in it is greater the more branched the PE is. The degree of branching has almost no effect on the relative content of trans-vinylene double bonds, for during destruction at 360° for 4 hours approximately 30% of such bonds are formed in all three types of PE. The relative amount of vinylidene double bonds formed, on the contrary, depends noticeably on the degree of branching of the PE: the more branched the PE, the more vinylidene double bonds are formed in it.

The ratio of the number of trans-vinylene bonds formed during destruction to vinylidene bonds, $N_{\mathrm{RCH=CHR}}/N_{\mathrm{R_2C=CH_2}}$, for the most highly branched PEVD is 1.2, while for RPE this ratio is 1.4. In PEND the ratio $N_{\mathrm{RCH=CHR}}/N_{\mathrm{R_2C=CH_2}}$ increases to 4.2. However, in this case such a large difference in the relative amount of double bonds of different types formed may be due to the presence of traces of catalyst or of products of its decomposition—aluminum and titanium oxides—since when destruction is carried out under the same conditions with unpurified PEND, 90% of the double bonds formed in it are of the trans-vinylene type. The data on the destruction of PEND contained in Table 1 were obtained for samples that had been reprecipitated several times from solution in toluene and then thoroughly dried.

Fig. 1. IR spectrum in the region 1700—1500 cm^{-1} of PEND (d = 0.25 mm), original (1), pyrolyzed at 360° for 4 hours in vacuum (2), and RPE (d = 0.25 mm), original (3), pyrolyzed at 360° for 4 hours in vacuum (4).

To check the influence of catalyst decomposition products on the course of PE destruction, we carried out pyrolysis at 360° for 4 hours of PEVD that had been mixed with titanium oxide (1% by weight), freshly prepared by precipitating

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Figure 1: Figure 1. IR spectrum in the region 1700-1500 cm^{-1} of PEND (d = 0.25 mm), original (1), pyrolyzed at 360° for 4 h in vacuum (2), and RPE (d = 0.25 mm), original (3), pyrolyzed at 360° for 4 h in vacuum (4).

Figure 2. IR spectrum of PEVD (d = 0.04 mm), pyrolyzed at 415° for 3 h in vacuum.

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an alcohol solution of $TiCl_4$ in benzene. The amount of trans-vinylene bonds formed proved to be the same as when pure PEVD was pyrolyzed under the same conditions, while the number of vinyl and vinylidene double bonds proved to be the same as in the initial PE, i.e., their amount did not increase during pyrolysis. Consequently, traces of catalyst decomposition products strongly influence the course of the thermal destruction of PE.

Fig. 2. IR spectrum of PEVD ($d = 0.04$ mm), pyrolyzed at 415° for 3 hours in vacuum.

With increasing time of pyrolysis at 360°, and also with increasing pyrolysis temperature, the relative amount of double bonds of the trans-vinylene type increases, and during pyrolysis at 415° for 3 hours bonds of this type constitute 50% of all double bonds formed during destruction both in PEND and in PEVD. Such an increase in the relative–

The decrease in the relative amount of double bonds of the trans-vinylene type with increasing degree of PE degradation can be explained by a number of reasons.

First, as the degree of PE degradation increases and molecules with double bonds at the ends accumulate in it, polymerization processes become more probable; as a result of these processes, terminal double bonds should disappear. The participation of double bonds in the middle of the chain, however, is much less probable in these processes, and therefore trans-vinylene double bonds will accumulate in the system. The presence of traces of catalyst in the polymer should accelerate polymerization reactions and promote more rapid disappearance of terminal double bonds. An increase in the probability of polymerization processes may be one of the reasons for the slowing of the rate of PE degradation at higher stages of its pyrolysis (5). Second, as the pyrolysis temperature increases, secondary reactions may occur directly with elimination of hydrogen and with formation of a double bond in the middle of the chain. This is confirmed by the fact that up to 25% hydrogen has been found in the gaseous products of thermal degradation of PE at temperatures above 400° (6).

In addition to branch points, "weak" sites in the PE molecule, where the CH bond can break preferentially compared with other sites, are CH bonds adjacent to double bonds (7). Rupture of such bonds leads to the appearance of allylic radicals and conjugated double bonds of the vinylene type. Absorption bands corresponding to the valence vibrations of $C = C$ in systems with conjugated double bonds lie in the region of 1600 cm^{-1} (8). In the spectra of the initial PE samples (Fig. 1), two very weak and diffuse absorption bands, 1595 and 1640 cm^{-1}, are observed in this region, and they are most intense in the HPE spectrum. In the spectra of PEND and PEVD pyrolyzed at 360° for 4 h, the optical density of the 1595 cm^{-1} band increases almost twofold. The intensity of the band in the region of 1640 cm^{-1} increases strongly owing to an increase in the number of terminal double bonds, the frequencies of whose valence vibrations lie in this region. After bromination of these PE samples, all bands related to double bonds disappear from their spectra; the band in the region of 1595 cm^{-1} also disappears, but a more intense and broad band appears in the region of 1650 cm^{-1}. It is known that upon bromination of butadiene, addition of bromine occurs in the 1,4 position, and as a result butyl bromide is obtained, in whose spectrum the band in the region of 1655 cm^{-1} corresponds to the valence vibration of the double bond (9). The disappearance of the 1595 cm^{-1} absorption band and the appearance of a band in the region of 1650 cm^{-1} in the spectrum of brominated PE is evidence that the absorption band in the region of 1595 cm^{-1} in the PE spectrum should be assigned to the valence vibrations of $C = C$ in conjugated systems. On this basis it may be concluded that, during thermal degradation of PE, conjugated double bonds are formed. The presence of dienes in the gaseous products of PE pyrolysis has already been shown in work (10).

In the spectra of the initial PE samples, the intensity of the 1595 cm^{-1} band is equal to or even greater than the intensity of the 966 cm^{-1} band. This indicates that the double bonds entering into the indicated conjugated systems in the initial PE either have a cis arrangement of hydrogen atoms or are located at chain-branching sites. With increasing time and temperature of thermal degradation, the intensity of the 1595 cm^{-1} band ceases to increase, its contour broadens into the 1600 cm^{-1} region, and at high degrees of degradation its maximum shifts into the region of 1606 cm^{-1}. The intensity of the 1606 cm^{-1} band increases as the degree of degradation increases and as the color of the polymer deepens to dark brown. Together with the 1606 cm^{-1} band, bands at 1135–1150, 1030, 845, 806–820, and 770 cm^{-1} appear in the spectrum of strongly degraded PE (Fig. 2). Intense bands in these regions are observed in the spectra of benzene derivatives and polyphenyls (11), as well as in the spectra of polyenes (12). In the electronic spectrum of pyrolyzed PE, the boundary of continuous absorption shifts into the visible region.

All this gives grounds to assume that, during the thermal destruction of PE, polyene and polyphenylene systems are formed in it. Evidently, the formation of polyphenylene and polyene systems accounts for the appearance of coloration in pyrolyzed PE, and is also the initial stage of carbonization of the polymer.

Fig. 3. IR spectrum of HDPE (d = 0.25 mm), pyrolyzed at 400° for 5 h; 1—not freed, 2—freed of the volatile fraction

Figure 3: Fig. 3. IR spectrum of HDPE (d = 0.25 mm), pyrolyzed at 400° for 5 h; 1—not freed, 2—freed of the volatile fraction

In the spectrum of HDPE (Fig. 3) subjected to thermal destruction at 400° for 5 h and then freed of volatile fractions at 100° in a high-vacuum apparatus (10^{-4} mm Hg), the intensity of the absorption bands at 1606, 1150, 1030, and 840—750 cm^{-1} is greater than in the spectrum of the sample not freed of the volatile fraction. Consequently, in the higher-molecular-weight fraction of the pyrolyzed sample the amount of polyphenylene and polyene systems is greater than in the lower-molecular-weight fraction. In the lower-molecular-weight fraction there are more terminal double bonds and relatively fewer trans-vinylene double bonds. This fact gives grounds for the conclusion that the formation of polyene chains and phenyl rings in PE during its thermal destruction acts similarly to the introduction of stabilizers into the polymer, and this may be one of the reasons for the decrease in the rate of destruction as it proceeds.

Fig. 3. IR spectrum of HDPE ($d = 0.25$ mm), pyrolyzed at 400° for 5 h;
1 —not freed, 2 —freed of the volatile fraction

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REFERENCES

1. W. G. Oakes, R. B. Richards, *J. Chem. Soc.*, **1949**, 2929.
2. L. H. Cross, R. B. Richards, H. A. Willis, *Disc. Farad. Soc.*, **9**, 235 (1950).
3. E. Barello, C. Mussy, *J. Polymer Sci.*, **13**, 402 (1954).
4. D. C. Smith, *Ind. and Eng. Chem.*, **48**, 1161 (1956).
5. H. Grassie, *Chemistry of the Processes of Polymer Destruction*, Moscow, 1959.
6. M. S. Khloplyankina, M. B. Neiman, V. D. Moiseev, *Plastics*, **2**, 9 (1961).

7. C. R. Poole, R. S. Anderson, *J. Chem. Phys.*, **31**, 346 (1959).
8. E. R. Blout, M. Fields, R. Karplus, *J. Am. Chem. Soc.*, **70**, 194 (1948).
9. Ya. M. Slobodyan, *ZhOKh*, **24**, 453 (1954).
10. L. A. Wall, C. L. Madorsky et al., *J. Am. Chem. Soc.*, **76**, 3430 (1954).
11. C. G. Cannon, *GBBM Sutherland Spectrochim. Acta*, **4**, 373 (1951).
12. K. Lunde, L. Zechmeister, *J. Am. Chem. Soc.*, **77**, 1647 (1955).

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