Thermoanalytical Studies of the Thermal Stability of High Polymers. II. The Differential Thermal Analysis and Thermogravimetric Analysis of Some Polyethylenes[*]

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Previous investigations of the thermal decomposition of high polymers have dealt almost entirely with isothermal experiments using thermobalance[1-5] to record the change in the weight of the sample at elevated temperatures. Recently the melting behavior and thermal changes of high polymers during oxidation or degradation have been investigated by differential thermal analysis,[6-10] and the thermal stability of linear polymers has been studied by thermogravimetric analysis.[11-17]

Although Paulik et al.[12] reported some thermoanalytical results on polyethylenes obtained by using the Derivatograph, the kinetic parameters for the thermal decomposition of polyethylenes were not determined. Anderson and Freeman[11] evaluated the activation energy and order of reaction for the thermal decomposition of a high-pressure polyethyene from the derivative thermogravimetric analysis curve, in which the rate of the weight loss of the sample is plotted against the temperature of a furnace at a constant rate of heating.

In the first paper of this series[18] an automatic recording thermobalance for studying the thermal stability of high polymers was described and a thermoanalytical study of the thermal decomposition of a commercial low-pressure polyethylene was presented.

It is the purpose of this paper to examine the thermal stability of some polyethylenes, when they are heated at a constant rate of 1°C/min., by differential thermal analysis and by thermogravimetric analysis, both in air and in a nitrogen atmosphere.

Experimental

Materials.—The polymers used were the low-pressure polyethylenes Hizex 5000 and 7000, supplied by the Mitsui Chemical Co., and the high-pressure polyethylenes Sumikathene MF-40 and F-70-6, produced by the Sumitomo Chemical Co. The materials were purified by precipitation using xylene as a solvent and methyl alcohol as a precipitant at room temperature and were then dried at about 60°C in vacuo for about 24 hr.

The melting point of the paraffin used is 56.0∼56.5°C.

Differential Thermal Analysis.—The apparatus which has been described in the previous paper[19] was used. Concentric cylindrical sample cells of stainless steel were used; they were essentially similar to that described by Vold.[20] The diameter and the depth of the sample cell are 1.5 cm. and 5 cm. respectively. The sample was put into the gap between the external sample holder and the concentric internal cylinder. Within the hollow of the internal cylinder, a two-junction chromel-constantan thermocouple was inserted in order to measure the temperature difference between the sample and the reference substance. The thermoelectric output was amplified and recorded on the chart of an electric recorder.

The temperature of the vertical electric furnace was automatically controlled so as to increase at a constant rate of about 1°C/min., and it was measured by means of another thermocouple of chromel-alumel and recorded on the same chart.

The sample weight used was about 1 g., a calcined alumina was used as the inert reference substance.

Experiments were carried out both in air and in a nitrogen atmosphere.

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1) N. Grassie, "The Chemistry of High Polymer Degradation Processes," Butterworths, London (1956).

2) H. H. Jellinek, *J. Polymer Sci*, **4**, 13 (1949).

3) S. L. Madorsky and S. Straus, *J. Res. Natl. Bur. Stands.*, **53**, 361 (1954).

4) S. L. Madorsky, ibid., **62**, 219 (1959).

5) L. A. Wall and S. Straus, *J. Polymer Sci.*, **44**, 313 (1960).

6) B. Ke, ibid., **42**, 15 (1960).

7) B. Ke, ibid., **61**, 47 (1962).

8) B. Ke, ibid., **A1**, 1453 (1963).

9) F. Danusso and G. Polizzotti, *Chim. e Ind.* (*Milan*), **44**, 241 (1962).

10) A. Rudin, H. P. Schreiber and M. H. Waldman, *Ind. Eng. Chem.*, **53**, 137 (1961).

11) D. A. Anderson and E. S. Freeman, *J. Polymer Sci.*, **54**, 253 (1961).

12) J. Paulik, H. Macskâsy, F. Paulik and L. Erdey, *Plaste und Kautschuk*, **8**, 588 (1961).

13) B. Kaesche-Krischer and H. J. Heinrich, *Z. physik. Chem., Neue Folge*, **23**, 292 (1960).

14) J. B. Gilbert, J. J. Kipling, B. McEnancy and J. N. Sherwood, *Polymer*, **3**, 1 (1962).

15) H. Anderson, *Makromolek. Chem.*, **51**, 233 (1962).

16) I. J. Goldfarb, R. J. McHenry and E. C. Penski, *J. Polymer Sci.*, **58**, 1283 (1962).

17) A. R. Shultz, N. Knall and G. A. Morneau, ibid., **62**, 211 (1962).

18) H. Kambe and S. Igarashi, *Report of Aeronaut. Res. Inst., the Univ. of Tokyo*, **28**, No. 376, 145 (1963).

19) H. Kambe, T. Ozawa, M. Onoue and S. Igarashi, This Bulletin, **35**, 81 (1962).

20) M. J. Vold, *Anal. Chem.*, **21**, 683 (1949).

Thermogravimetric Analysis. — An automatic recording thermobalance, which had been designed and constructed in our laboratory[18] using a calibrated phosphor-bronze spring and a linear variable differential transformer, was used to record the change in the weight of the sample, while the furnace temperature was continuously elevated at a constant rate of about 1°C/min., in air and in a nitrogen atmosphere. The temperature of the cylindrical electric furnace was controlled by an electronic program controller.

The temperature of the sample was measured by means of a chromel-alumel thermocouple located near the sample glass crucible; the output of this thermocouple was recorded. The diameter and the depth of the crucible were 1.1 cm. and 1.0 cm. respectively. The sample weight used was about 90 mg.

Results and Discussion

Differential Thermal Analysis.—Typical results of the differential thermal analysis curves for some polyethylenes are shown in Fig. 1. In these curves the differential temperature between the sample and the reference substance is plotted against the reference temperature.

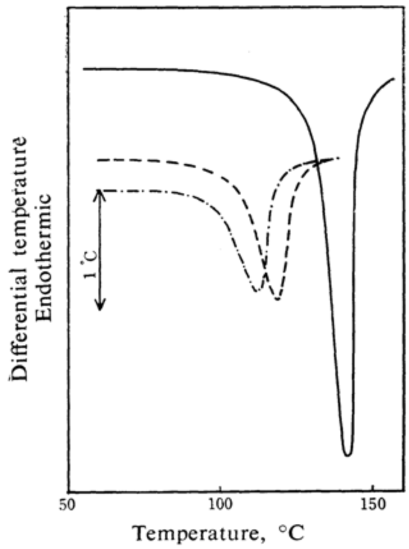

Fig. 1. Differential thermal analysis curves for polyethylenes. Solid line, Hizex 7000; dashed line, Sumikathene MF-40; chain line, Sumikathene F-70-6.

A low-pressure polyethylene, Hizex 7000, displayed a sharp endothermic peak over the range from 120 to 145°C. Two high-pressure polyethylenes, Sumikathene MF-40 and F-70-6, showed a small peak over the ranges from 103 to 118°C and from 103 to 112°C respectively. It is evident that each endothermic peak corresponds to a melting point of the polymer.

The area of a peak in the differential thermal analysis curve is proportional to the amount of the absorbed (or evolved) heat in the sample, and it can be calibrated by a known heat. When the heat of fusion for benzoic acid was used as a standard for calibration, the heats of fusion for these polymers were obtained as follows: 51 cal./g. for Hizex 7000, 42 cal./g. for Hizex 5000, 24 cal./g. for Sumikathene MF-40 and 22 cal./g. for Sumikathene F-70-6. Dividing these values by the heat of fusion for a perfectly crystalline polyethylene (i. e., 66 cal./g.[21]), the crystallinity of each sample was obtained. These values are listed in Table I. It is clear that the crystallinity of the branched high-pressure polyethylene is smaller than that of the low-pressure polymer. The results are in agreement with the work of Ke.[6] In Table I the crystallinity of the polymer is shown to be smaller than the reported values of Hizex 5000 and 7000 (e. g., 80~90%). However, according to the theory of differential thermal analysis,[22] the area of a peak depends not only on

TABLE I. DIFFERENTIAL THERMAL ANALYSIS OF POLYETHYLENES

Polymer	M. p. °C	Heat of fusion cal./g.	Crystallinity %	Entropy of fusion e. u./g.
Sumikathene				
F-70-6	103~112	22	33	0.057
MF-40	103~118	24	36	0.062
Hizex				
5000	122~140	42	64	0.102
7000	120~145	51	77	0.123

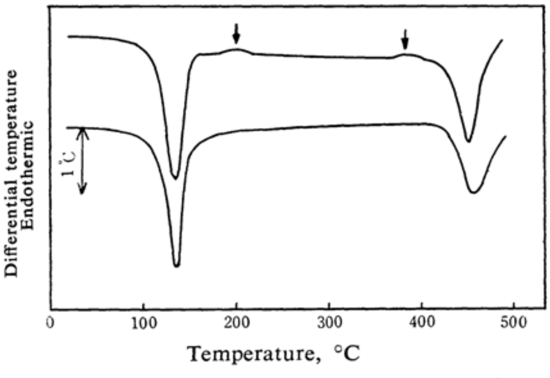

Fig. 2. Differential thermal analysis curves for low-pressure polyethylene Hizex 5000. Upper curve, in air; lower curve, in a nitrogen atmosphere.

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[21] M. Dole, W. P. Hettinger, Jr., N. R. Larson and J. A. Wethington, Jr., *J. Chem. Phys.*, **20**, 781 (1952); M. Dole and B. Wunderlich, *J. Polymer Sci.*, **24**, 139 (1957).

[22] W. J. Smothers, "Differential Thermal Analysis: Theory and Practice," Chemical Publishing Co., Inc., New York (1958), p. 85.

the amount of the absorbed heat, but also on the thermal conductivity of the sample. Since the latter value is not kept constant over the melting range in the polymer, it should be noticed that the latent heat (or crystallinity) obtained from the data of the differential thermal analysis may be the apparent value.

In his earlier work Ke⁶⁾ observed that the crystallinity of commercial polyethylene estimated by differential thermal analysis agreed well with the reported one determined by the X-ray method; however, he has recently reported⁷⁾ that there was a considerable discrepancy between the two crystallinities of the ethylene copolymers. Therefore, it may be suggested that this discrepancy between the crystallinity evaluated by differential thermal analysis and the reported value may be due to the difference in methods.

Figure 2 shows the differential thermal analysis curves for a low-pressure polyethylene, Hizex 5000, in air and in a nitrogen atomsphere from the ambienat temperature to approximately 500°C. The upper curve in Fig. 2 shows two endothermic peaks at 135 and 457°C. The former peak for the melting of the sample agrees with the literature value of 135°C. The latter peak at 457°C is due to the thermal decomposition of polyethylene, which will be discussed in the following section.

Two small exothermic peaks, indicated by arrows, show the oxidation of polyethylene, because these exothermic peaks are not observed in the lower curve in a nitrogen atmosphere.

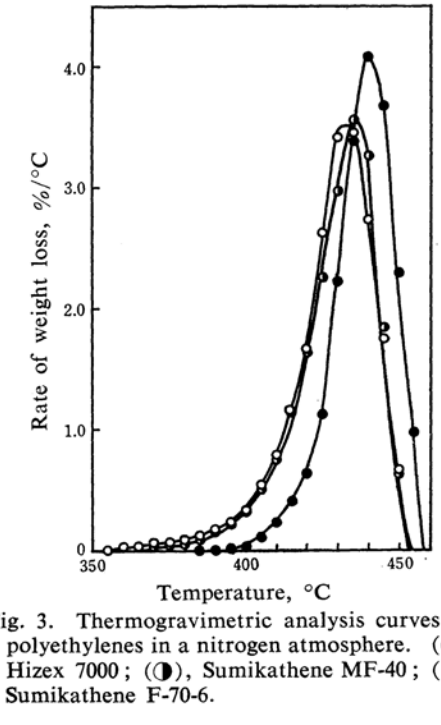

Fig. 3. Thermogravimetric analysis curves for polyethylenes in a nitrogen atmosphere. (●), Hizex 7000; (◑), Sumikathene MF-40; (○), Sumikathene F-70-6.

In the differential thermal analysis curve of low-pressure polyethylene in the presence of air, a small exothermic peak has been observed by Paulik et al.¹²⁾ in the range from 190 to 250°C. Danusso et al.⁹⁾ have also reported that, after the melting of the polyethylene, an exothermic peak due to oxidation was observed in the differential thermal analysis curve in air.

By a gas-flow-type differential thermal analysis apparatus recently constructed in our laboratory, it has been observed that the crystallinity of polyethylene decreases abruptly in the first exothermic stage (ca. 180°C). The results will be reported elsewhere.

Thermogravimetric Analysis in Nitrogen. — The thermogravimetric analysis curves for Hizex 7000, Sumikathene MF-40 and Sumikathene F-70-6 in a nitrogen atmosphere are shown in Fig. 3. These curves, in which the rate of weight loss (%/°C) is plotted against the temperature, were obtained by a graphical differentiation of the curve of weight loss as a function of the temperature.

From Fig. 3 it is clear that thermal decomposition for each sample takes place in one stage. The weight losses of the two high-pressure polyethylenes, Sumikathene MF-40 and F-70-6, commence at approximately 360°C, and the weight losses for these polymers reach a maximum rate (ca. 3.5%/°C) at about 435°C. However, the thermal decomposition of the low-pressure polyethylene, Hizex 7000, takes place over the range from 380 to about 455°C. The temperature at which the thermal decomposition of high-pressure polyethylene commences is obviously higher by about 20°C

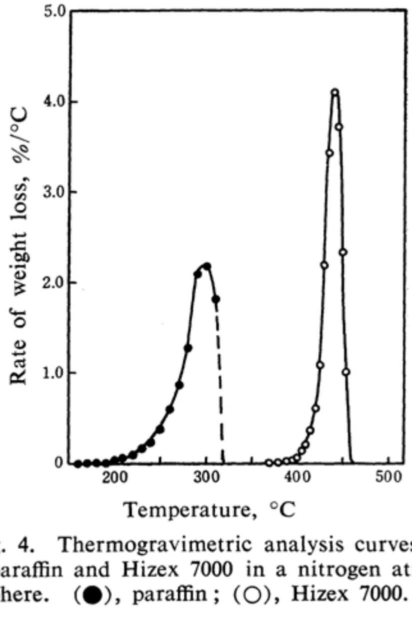

Fig. 4. Thermogravimetric analysis curves for paraffin and Hizex 7000 in a nitrogen atmosphere. (●), paraffin; (○), Hizex 7000.

than that of low-pressure polyethylene.

The above results obtained from the thermogravimetric measurements support the conclusion that a branched polyethylene is thermally more unstable than a linear one in isothermal experiments[5] because thermal decomposition is initiated at the branched point with a tertiary hydrogen atom.

Paulik et al.[12] have reported thermogravimetric studies of polyethylenes including low-pressure, medium-pressure and high-pressure samples in air and in a nitrogen atmosphere. However, they have not described the thermal stability of these polymers in a nitrogen atmosphere. It seems to be impossible in a nitrogen atmosphere for the Derivatograph to clarify the differences in the chemical structure of commercial polyethylenes.

In Fig. 4 the derivative thermogravimetric analysis curves for paraffin (m. p. 56.0～56.5°C) and polyethylene (Hizex 7000) are shown. Figure 4 shows that the weight loss of paraffin begins slowly at about 180°C and that that of polyethylene begins at 380°C. The degradation products were collected into the trap which was set below the sample crucible. The melting points of the trapped products for paraffin and polyethylene were 55.0～55.5°C and 51.0～67.0°C respectively. Since the melting point of the trapped products for paraffin corresponds well with the original one, it is confirmed that the weight loss of paraffin is mainly due to the vaporization of the sample. When the melting point of the trapped paraffin is compared with that of the degradation products for polyethylene, it is also confirmed that the thermal decomposition of polyethylene occurs at the peak appearing in the derivative thermogravimetric analysis curve.

Madorsky et al.,[23] when investigating the degradation products for polyethylene by means of a mass spectrometer, have found that the products contained very little monomer but mainly paraffins and olefins with up to about fifty carbon atoms. As has been mentioned above, the degradation products for Hizex 7000 melts over a wide range in temperature. This means that the products contain a number of hydrocarbon members.

The apparent activation energy and the order of reaction for the thermal decomposition of polymers in a nitrogen atmosphere were evaluated from the derivative thermogravimetric analysis curve by the method of Freeman and Carroll.[24] They derived the following equation:

$$\Delta \log(\mathrm{d}W/\mathrm{d}T)/\Delta \log W_r = n - (E/2.3\boldsymbol{R}) \times \Delta(1/T)/\Delta \log W_r$$

where $\mathrm{d}W/\mathrm{d}T$ is the rate of change in weight, n is the order of reaction, E is the apparent activation energy, $\boldsymbol{R}$ is the gas constant, T is the absolute temperature, and W_r is the weight of the reactant at the temperature, T. If we plot $\Delta \log(\mathrm{d}W/\mathrm{d}T)/\Delta \log W_r$ against $\Delta(1/T)/\Delta \log W_r$, we obtain a linear plot with an intercept, n, on the ordinate and slope equal to $E/2.3\boldsymbol{R}$. This plot for the thermal decomposition of the low-pressure polyethylene Hizex the 7000 is shown in Fig. 5. Thus we found that $E=73.6$ kcal./mol. This agrees with the value of 72 kcal./mol. for the polymethylene of Madorsky.[4] The order of reaction for this stage was not clear. The results are listed in Table II.

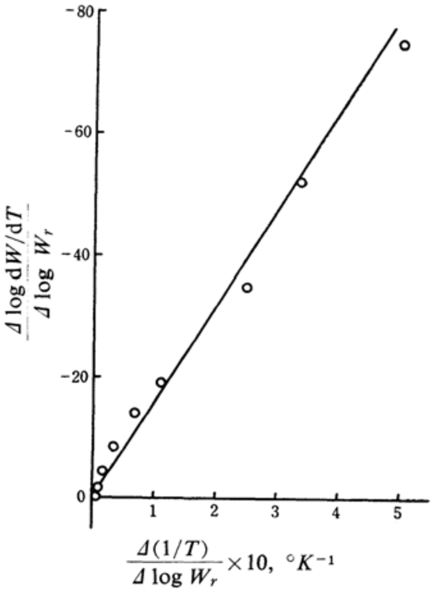

Fig. 5. Freeman's plot for thermal decomposition of low-pressure polyethylene Hizex 7000.

TABLE II. THERMOGRAVIMETRIC ANALYSIS OF POLYETHYLENES IN NITROGEN ATMOSPHERE

Polymer	Decomp. temp. °C	Apparent activation energy kcal./mol.	Residue %
Sumikathene			
F-70-6	360～450	74	0
MF-40	360～450	61	0
Hizex			
7000	380～450	74	0

Anderson and Freeman[11] have studied thermogravimetrically the thermal decomposition of high-pressure polyethylene (DYNH) in vacuo. They have established that the thermal

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[23] S. L. Madorsky, S. Straus, D. Thompson and W. Williamson, *J. Res. Natl. Bur. Stands.*, **42**, 499 (1949).

[24] E. S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).

TABLE III. THERMOGRAVIMETRIC ANALYSIS OF POLYETHYLENES IN AIR

Polymer	Decomp. temp. °C	Weight loss at 1st stage %	2nd stage %	3rd stage %	Residue %
Sumikathene					
F-70-6 (purified)	190~440	8.8*	13.2	74.0	4.0
F-70-6 (unpurified)	210~450	4.3	26.8	66.6	2.3
Hizex					
7000	250~450	2.6	21.6	73.0	2.8

* Estimated value

decomposition of the polymer takes place in three stages; the initial, 3% zero-order reaction, the second, 3 to 15% zero-order stage, and the final, first-order reaction, occurring above 35% degradation. The energies of activation for the stages are 48 kcal./mol., 61 kcal./mol. and 67 kcal./mol. respectively.

Thermogravimetric Analysis in Air. — The thermogravimetric analysis curves for Hizex 7000, Sumikathene F-70-6 (unpurified) and Sumikathene F-70-6 (purified) in air are shown in Fig. 6. The curves are different from that obtained in a nitrogen atmosphere (Fig. 3).

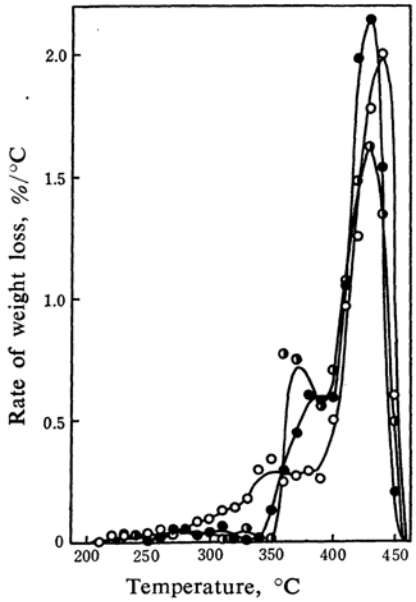

Fig. 6. Thermogravimetric analysis curves for polyethylenes in air. (●), Hizex 7000; (◑), Sumikathene F-70-6 (unpurified); (○), Sumikathene F-70-6 (purified).

The weight loss of Sumikathene F-70-6 commences at about 200°C, and that of Hizex 7000, at 250°C. The maximum rates of weight loss of these polymers occur at about 430°C. In these curves it seems that the oxidative degradation takes place in three stages: the first, up to approximately 350°C, the second from 350 to about 390°C, and the third from 390 to about 455°C.

When the curve for the purified Sumikathene is compared with that for the unpurified one, it is found that the weight loss for the first stage of the latter is smaller than for that of the former. This may indicate the effect on the theraml stability exerted by an antioxidant added to the commercial polymer. In the lower-temperature range the weight loss is mainly due to the degradation at the branching point in the polymer molecule. In accordance with this, the weight loss of the less-branched Hizex 7000 in this stage is smaller than that of Sumikathene. In a previous paper[25] it has also been recognized that the chain branching and the unsaturation have a marked effect on the weight loss at the first stage of the oxidative degradation of the irradiated polyethylene.

Paulik et al.[12] observed from the Derivatograph of the low-pressure polyethylene that the weight gain of the sample took place in the range from 160 to 200°C and that the rapid oxidative weight loss occurred over the range from 320 to about 400°C.

Since the oxidative degradation of the polymer may begin at its surface, the influence of the surface area of the sample on the weight loss in the thermogravimetric analysis was examined. For this purpose the sample crucible, the surface area of which is 1.63 times that of the crucible usually used, was utilized for low-pressure polyethylene. As a result, it was recognized that the weight loss at the low-temperature stage increased to 1.4 times the value obtained with the usual crucible.

Summary

The thermal stability of polyethylenes has been studied by differential thermal analysis and by thermogravimetric analysis in air and in a nitrogen atmosphere.

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[25] S. Igarashi, I. Mita and H. Kambe. *J. Appl. Polymer Sci.*, in press.

The crystallinities of some polyethylenes have been evaluated from the data of differential thermal analysis. These values are smaller than the reported value. This discrepancy may be due to differences in the methods.

In the differential thermal analysis curve for low-pressure polyethylene Hizex 5000 in air, two small exothermic peaks due to oxidation were observed at about 200 and at about 390°C. The endothermic peaks at 135 and at 457°C correspond to the melting and to the thermal decomposition points of polyethylene.

In thermogravimetric analysis in a nitrogen atmosphere, the thermal decomposition of low-pressure polyethylene takes place over the range from 380 to about 450°C, and that of high-pressure polyethylene, from 360 to about 450°C. In the presence of air, the oxidative degradation of low-pressure and high-pressure polyethylenes occurs in three stages: the first from about 200 to 350°C, the second from about 350 to 390°C, and the third from about 390 to 455°C.

It has been concluded that the thermal stability of high-pressure polyethylene is smaller than that of low-pressure polyethylene. This may be attributed to the difference in branching of commercial polyethylenes.

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