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OXIDATIVE DEGRADATION PRODUCTS OF IRRADIATED POLYETHYLENE

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ABSTRACT

Oxidative thermal degradation products of polyethylenes at various temperatures crosslinked with electron beams have been analyzed with gas chromatography and mass spectrometry techniques. Carbon monoxide and carbon dioxide are determined at a temperature range of 200–340°C, and the activation energies of the unirradiated and the irradiated polyethylene (at 100 Mrad) are 13.5 and 11.4 Kcal/mole, respectively. C_1 to C_8 hydrocarbons produced in air and in nitrogen are determined at temperatures from 400 to 450°C for the polyethylenes. The irradiated polyethylene produces less hydrocarbons in air than the unirradiated polyethylene, contrary to the fact that the crosslinked polymer evolves more hydrocarbons than the unirradiated polymer in a nitrogen atmosphere. Aldehydes and ketones are observed in the volatile oxidative degradation products, and these carbonyl compounds increase quantitatively with increase of temperature up to about 460°C. It is concluded that irradiated polyethylene is thermally more unstable in the absence of oxygen and more easily oxidable at low degradation temperatures in air than unirradiated polyethylene. Irradiated polyethylene, however, is more heat-stable than unirradiated polyethylene from the standpoint of the ignition process.

INTRODUCTION

In the previous paper[1], the thermal stability of polyethylenes irradiated with electron beams was demonstrated by softening point measurement, DTA and TG.

Decomposition products of polyethylene in the absence of oxygen have been determined by many investigators. A number of papers described the oxidative thermal degradation products of polyethylene, but as far as is known, there has been no investigation into the thermal degradation products of polyethylene crosslinked by irradiation.

Chaigneau and Moan[2] decomposed polyethylene in the presence of oxygen at 300 and 500 °C, and they found alkanes, alkenes and aromatic compounds besides hydrogen, carbon monoxide and carbon dioxide. Spore[3] identified fifteen kinds of aliphatic compounds and nine kinds of oxidized organic compounds at decomposition temperatures of 75–200 °C. In the course of oxygen absorption studies, Matveeva et al.[4] reported the volatile oxidation products of acids, carbonyl compounds, carbon monoxide, carbon dioxide, hydrogen and water.

The purpose of this investigation was to determine the oxidative degradation products of the irradiated polyethylenes using a gas chromatograph and a gas chromatograph–mass spectrometer combined system to give some relations between the degradation temperature and the quantity of the products.

EXPERIMENTAL

Materials and irradiation

The polyethylenes used and the irradiation techniques were the same as those mentioned in the previous paper[1]. The samples used in this report were cut by a punch to small disks (1.3 mm diameter, 0.2 mm thickness, about 0.35 mg each) from the microtomed polyethylene sheets.

Degradation system

The apparatus used for the degradation of the polymers is a commercial pyrolyzer (Shimadzu Seisakusho, Model PYR-1A) shown in Fig. 1. An aluminium cup (2 mm i.d., 1 mm depth) containing sample was placed in a quartz tube, which was connected to a gas chromatograph. The temperature on the quartz tube was controlled by an additional electronic controller giving a temperature stability of about 1 °C at 400 °C. About 10 sec are required to reach a preselected temperature after the insertion of the sample rod.

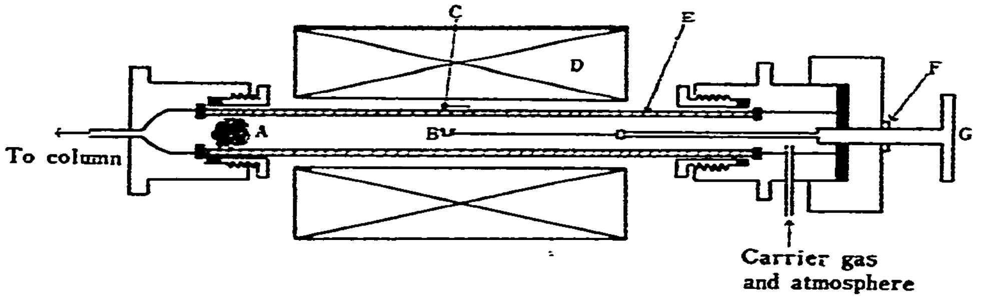

Fig. 1. Degradation system. A = Glass wool; B = sample cell; C = thermocouple; D = furnace; E = quartz tube; F = stopper; G = sample rod.

The quartz tube has a volume of about 6 ml. The outlet tube from the furnace is maintained at approximately 140 °C with electrical heating tape to avoid the absorption of oxidative products. Dried air was introduced into the quartz tube before every run. The degradation was carried out in a state of rest.

The furnace was set from 200 to 340 °C for each increase of 20 °C in temperature for the determination of carbon monoxide and carbon dioxide. The sample was decomposed in air for 20 min. For the determination of hydrocarbons and oxidized organic compounds, the furnace was set from 400 to 500°C for each increase of 10°C in temperature. The sample was decomposed in air for 30 sec. The thermal degradation of polyethylenes in nitrogen was also carried out to see the influence of oxygen at the temperature range from 460 to 540°C. The decomposition time was also 30 sec.

Chromatography and mass spectrometry

The gas chromatograph used was equipped as a dual column instrument. Carbon monoxide and carbon dioxide were separated using Molecular Sieve 5A and activated charcoal, respectively. They were monitored by thermal conductivity detection. The organic products were separated using Porapak Q and monitored by flame ionization detection. The operating conditions of the columns are:

(1) Molecular Sieve 5A and activated charcoal: 2 m × 3 mm i.d. in stainless steel, temperature at 50°C, helium carrier gas at 50 ml/min.

(2) Porapak Q: 2 m × 3 mm i.d. in stainless steel, temperature programmed from 40 to 240°C at 9.8°C/min, nitrogen carrier gas at 40 ml/min.

Many of the peaks were identified by comparing retention indices with those of pure materials. For quantitative analyses, calibration curves were prepared for carbon monoxide and carbon dioxide, and approximate substance correction factors were employed for the organic compounds[5] after measurement of peak areas.

Mass spectra were obtained using a Shimadzu-LKB gas chromatograph–mass spectrometer 9000. The degradation system for the polymer was also Shimadzu PYR-1A. Mass spectra were recorded at 20–70 eV and interpreted using the data compiled by Stenhagen et al.[6].

RESULTS AND DISCUSSION

Determination of CO and CO_2

Preliminary experiment was carried out to determine a heating time in the oxidative degradation system, and the experiment indicated that the quantity of CO formed during the oxidation became almost constant over 15 min at 250°C. A heating time of 20 min was adopted for the degradation in air from 200 to 340°C.

A few experimental results showing the amount of CO and CO_2 produced at various temperatures are shown in Figs. 2 and 3, for the unirradiated polyethylenes and the polyethylenes irradiated at 100 Mrad. They are reported in microliter per milligram of sample for the degradation time of 20 min, and are based on two or more repeat tests. Total amounts of CO and CO_2 for these samples are shown in Fig. 4.

From these results, it can be seen that the crosslinked polyethylenes are more easily oxidized than the unirradiated polyethylenes at temperatures below 300°C. This may be mostly due to the increase of tertiary carbon atoms resulting from crosslinking. However, the crosslinking effect is not observed as the temperature approaches the ignition region, because oxygen molecules attack the polymer chains at random in this temperature range.

The regularity in the production of CO and CO_2 might be related to the fact that a reproducible exothermic peak in DTA is observed for polyethylene at ca. 200–300 °C.

It can also be seen from the figures that the oxidation of the linear polyethylenes becomes more rapid than that of the branched polyethylenes. In the autoxidation processes, the tertiary carbon atoms in the branched polymer provide active sites and the highly branched part is oxidized initially. The branched polymer, however, is less oxidized in the oxidative degradation process because the branched polymer is presumably more easily crosslinked by heating to give a stable state than the linear polymer.

Measurement of activation energies

Arrhenius plots for the CO and CO_2 production for the polyethylenes are shown in Figs. 5 and 6. In the calculation of the activation energies, it was assumed that the oxidative degradation obeyed first-order kinetics and 1 mg of polyethylene evolved 1.6 ml of CO_2 after the complete thermal oxidation. Actually, the quantity of CO and CO_2 produced at 600 °C for 20 min was about 1.45 ml (Fig. 4).

The activation energies of the unirradiated polyethylenes and the polyethylenes irradiated at 20 and 100 Mrad were 13.5, 13.1 and 11.4 Kcal/mole, respectively. The activation energies, however, for the oxidative thermal degradation will be expected

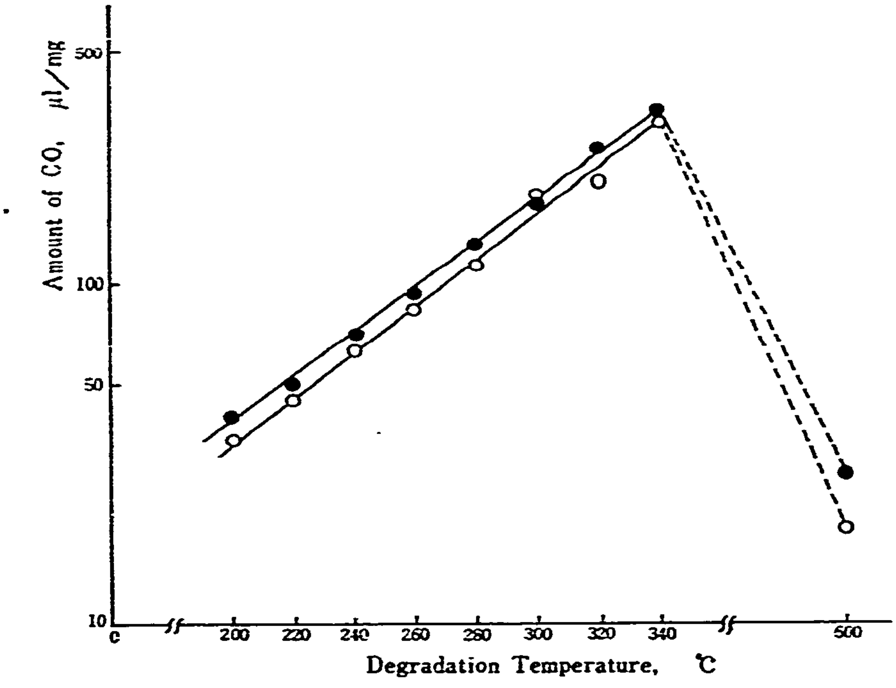

Fig. 2. Variation of the amount of carbon monoxide for polyethylenes irradiated at 100 Mrad with degradation temperature in air. (○) Low-density polyethylene; (●) high-density polyethylene.

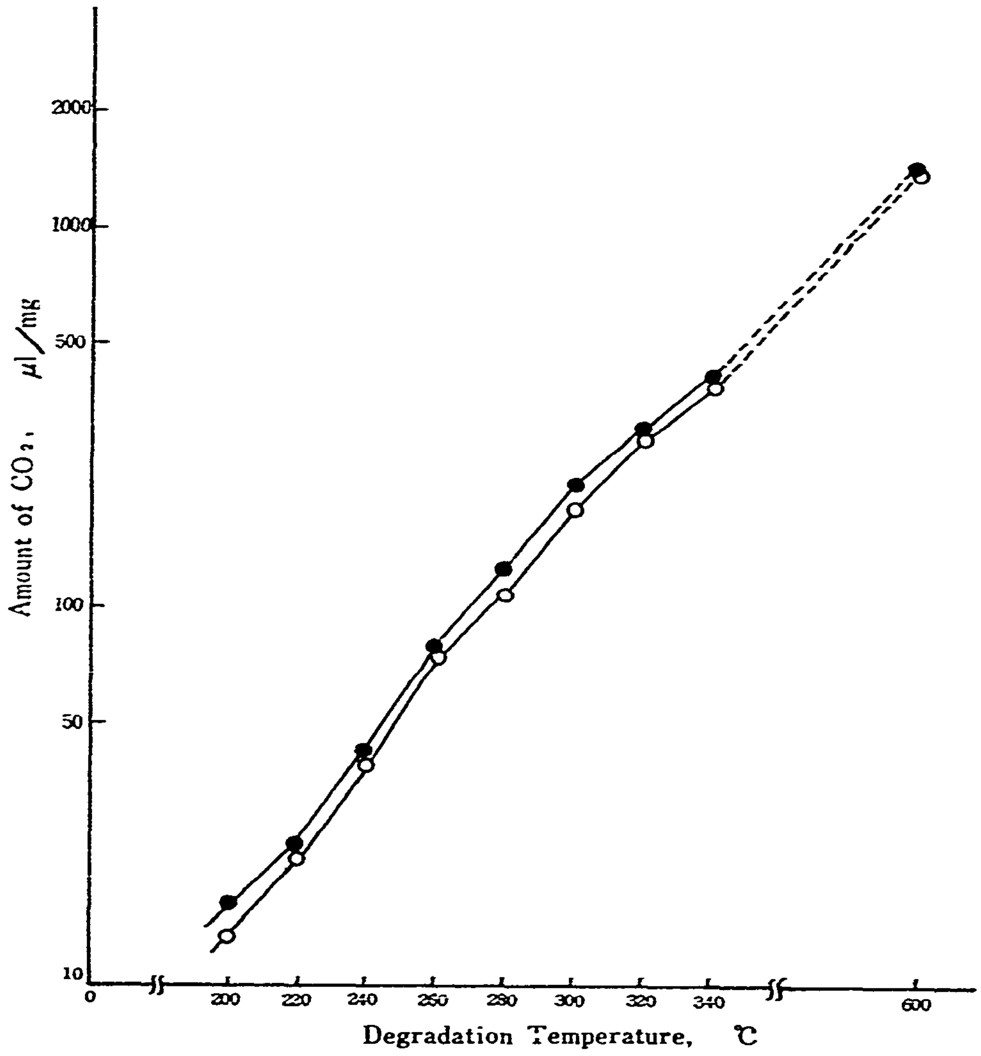

Fig. 3. Variation of the amount of carbon dioxide for unirradiated polyethylenes with degradation temperature in air. (○) Low-density polyethylene; (●) high-density polyethylene.

to have a little larger values than the values mentioned above, when the products water and a small amount of organic compounds are taken into consideration.

Grieveson et al.[7] found that at temperatures between 140 and 170 °C the activation energy of the reaction rate of oxidation of polyethylene was constant at 31 Kcal/mole, but above 170 °C it decreased progressively until the value was 15 Kcal/mole at 200 °C. Kotoyori[8] obtained 14.7 Kcal/mole for the activation energy of polyethylene using Kissinger's equation at temperatures between ca. 200 and 280 °C.

The activation energies of the branched and the linear polymers appear to be similar, assuming that the same type of oxidation mechanisms occurs in both cases.

Analysis of the products in nitrogen

The thermal degradation of polyethylene was carried out in nitrogen in order to be able to compare it with that in the presence of oxygen. Fig. 7a shows the chromatographic traces of the thermal degradation of the unirradiated low-density polyethylene at 540 °C. The numbers shown in the figure represent the number of carbon atoms of normal-chain hydrocarbons of the degradation products. It is assumed that each peak comprises alkanes, alkenes and alkadienes.

The degradation products of unirradiated low-density and irradiated low-density polyethylene (at 100 Mrad) are presented in Fig. 8. They were calculated as "mole per cent of the original polymer" (considered as the monomer, ethylene).

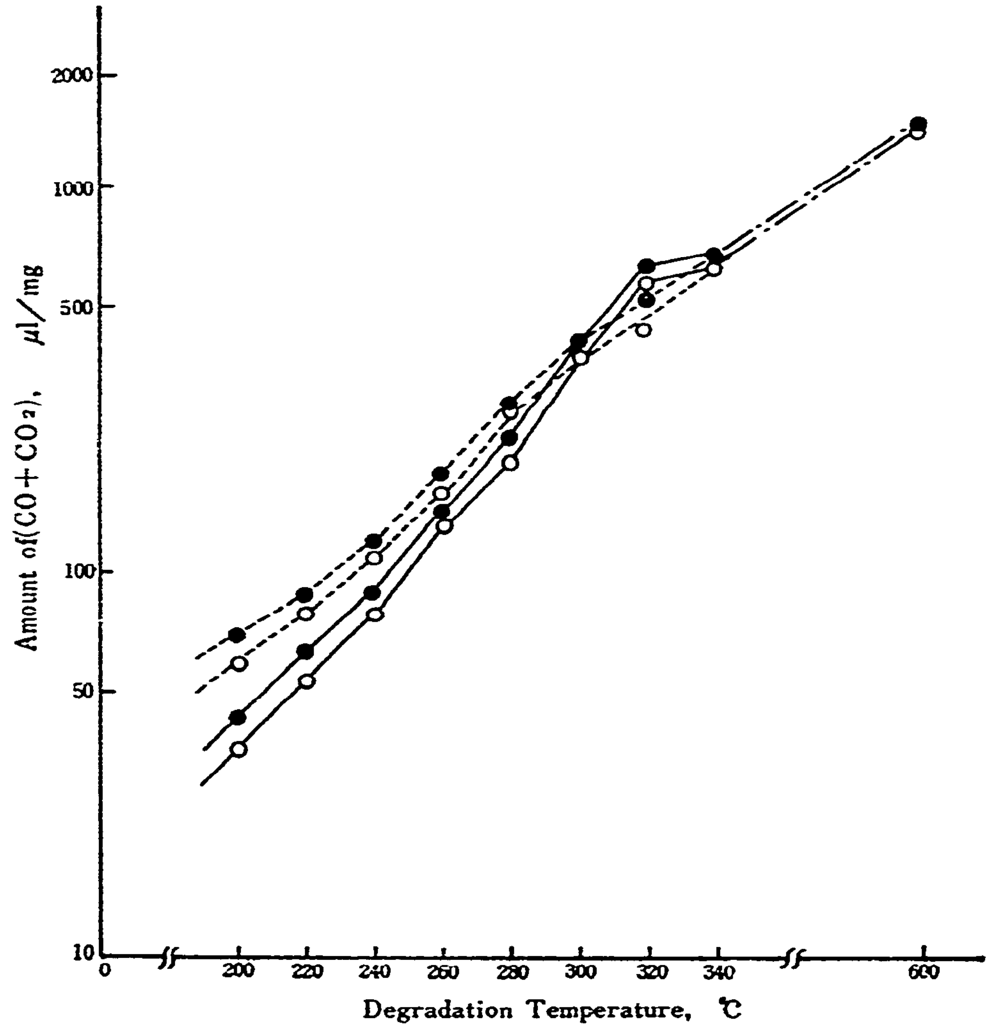

Fig. 4. Variation of the total amount of carbon monoxide and carbon dioxide for polyethylenes with degradation temperature in air. Straight line, unirradiated polyethylenes; dotted line, irradiated polyethylene at 100 Mrad. (○) Low-density polyethylene; (●) high-density polyethylene.

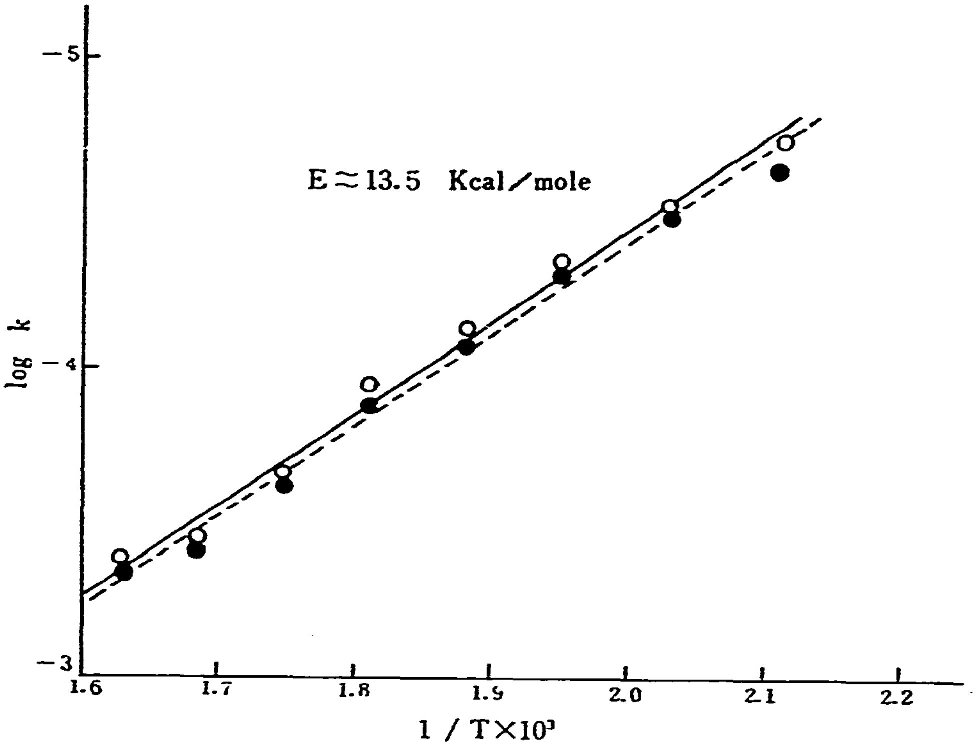

Fig. 5. Arrhenius plots for the production of carbon monoxide and carbon dioxide for unirradiated polyethylenes. (○) Low-density polyethylene; (●) high-density polyethylene.

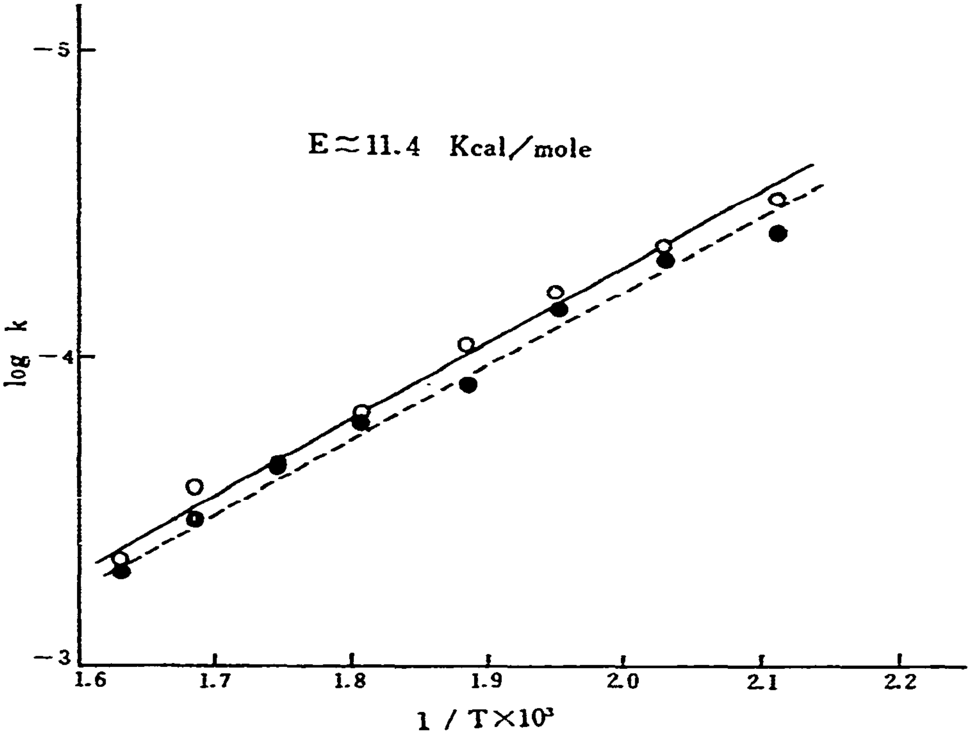

Fig. 6. Arrhenius plots for the production of carbon monoxide and carbon dioxide for irradiated polyethylenes at 100 Mrad. (○) Low-density polyethylene; (●) high-density polyethylene.

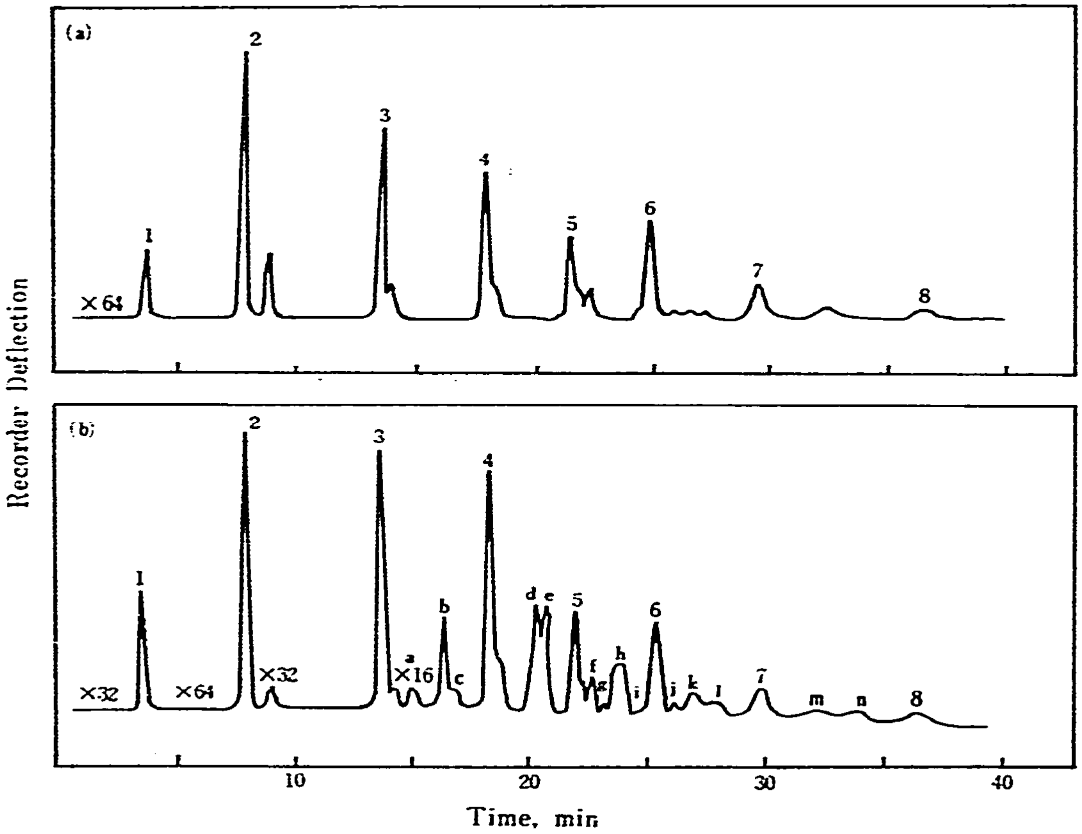

Fig. 7. (a) Chromatogram of the degradation products of unirradiated low-density polyethylene in nitrogen at 540°C. (b) Chromatogram of the oxidative degradation products of polyethylene irradiated at 100 Mrad in air at 460°C.

The quantity of ethylene found in the products is largest at the high pyrolysis temperatures. It is assumed that the main-chain scission of polymer molecules occurs easily at this temperature range and the products decompose to molecules of low molecular weight at the first stage[9]. The C_3 and C_6 hydrocarbons are assumed to be the most abundant volatile products at the low degradation temperatures. This result is in agreement with that of Tsuchiya and Sumi[10]. They explained this phenomenon from the standpoint of intramolecular transfer of radicals.

The thermal degradation mechanism of irradiated polyethylene appears to be the same as that of unirradiated polyethylene judging from the chromatographic traces. It is also shown from the quantities of hydrocarbons produced that irradiated polyethylene is thermally more unstable than unirradiated polyethylene.

Analysis of the products in air

In order to investigate the effect of oxygen on the degradation of the polyethylenes, the oxidative degradation of the polymers was carried out in air at temperatures of the combustion region. Most of the flammable gases evolved from polyethylene will be oxidized when exposed to air for a long time at temperatures over 400°C. The evolution of flammable gases, however, will be observed when exposed for a short period.

Fig. 7b shows the chromatographic traces of the thermal oxidative degradation of the irradiated low-density polyethylene (at 100 Mrad) at 460°C. The gas chromatogram of the unirradiated polymer was similar to that of the irradiated polymer. It is clear that certain peaks (from a to n, except f, j and m) are characteristic of the oxidative thermal degradation of polyethylene. Twenty-six peaks were found when

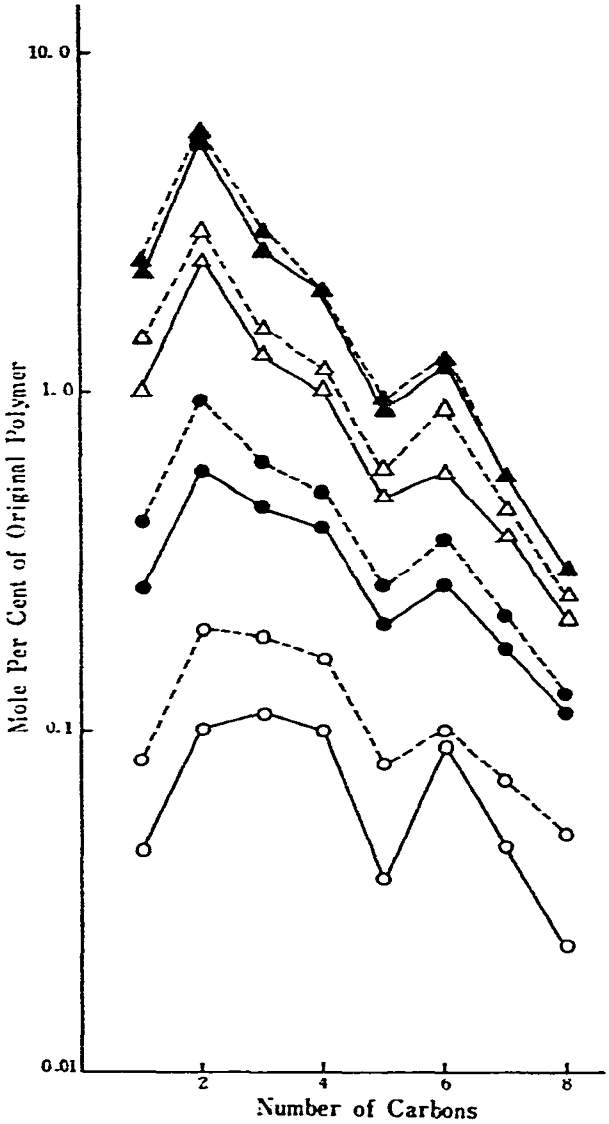

Fig. 8. Degradation products of polyethylenes in nitrogen. Straight line, unirradiated low-density polyethylene; dotted line, irradiated low-density polyethylene at 100 Mrad. (○) 460°C; (●) 480°C; (△) 400°C; (▲) 520°C.

the volatile products were separated with a Porapak Q column. All the peaks were also analyzed by the gas chromatograph–mass spectrometer, and hydrocarbons, aliphatic aldehydes and ketones were found. These oxidized organic compounds are specified in Table 1.

Fig. 9 shows the quantities of hydrocarbons produced by the oxidative degradation of unirradiated and irradiated polyethylene at various degradation temperatures. In Fig. 10, the variation in the amount of C_2 and C_3 hydrocarbons produced in air and in nitrogen is shown with increasing degradation temperature.

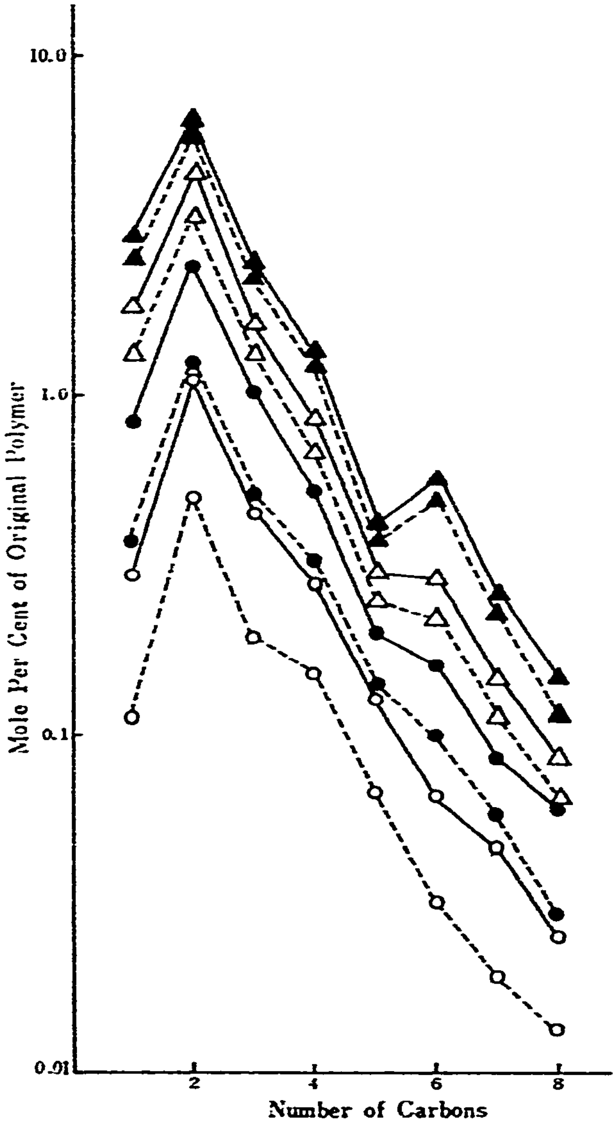

Fig. 9. Hydrocarbons produced by the oxidative degradation of polyethylenes in air. Straight line, unirradiated low-density polyethylene; dotted line, irradiated low-density polyethylene at 100 Mrad. (○) 410°C; (●) 430°C; (△) 450°C; (▲) 470°C.

TABLE 1

ANALYSIS OF OXIDIZED ORGANIC PRODUCTS OF POLYETHYLENE BY GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

Peak	*Oxidized organic products*	*b.p. (°C)*
a	Formaldehyde	−21
b	Acetaldehyde	21
c	Not identified	
d	Acrolein	52.5
e	Propionaldehyde	49
g	Not identified	
h	Methyl ethyl ketone	79.6
	Methyl vinyl ketone	79–80
i	Chrotonaldehyde	104
k	Valeraldehyde	120
l	Not identified	
n	Heptaldehyde	152.8

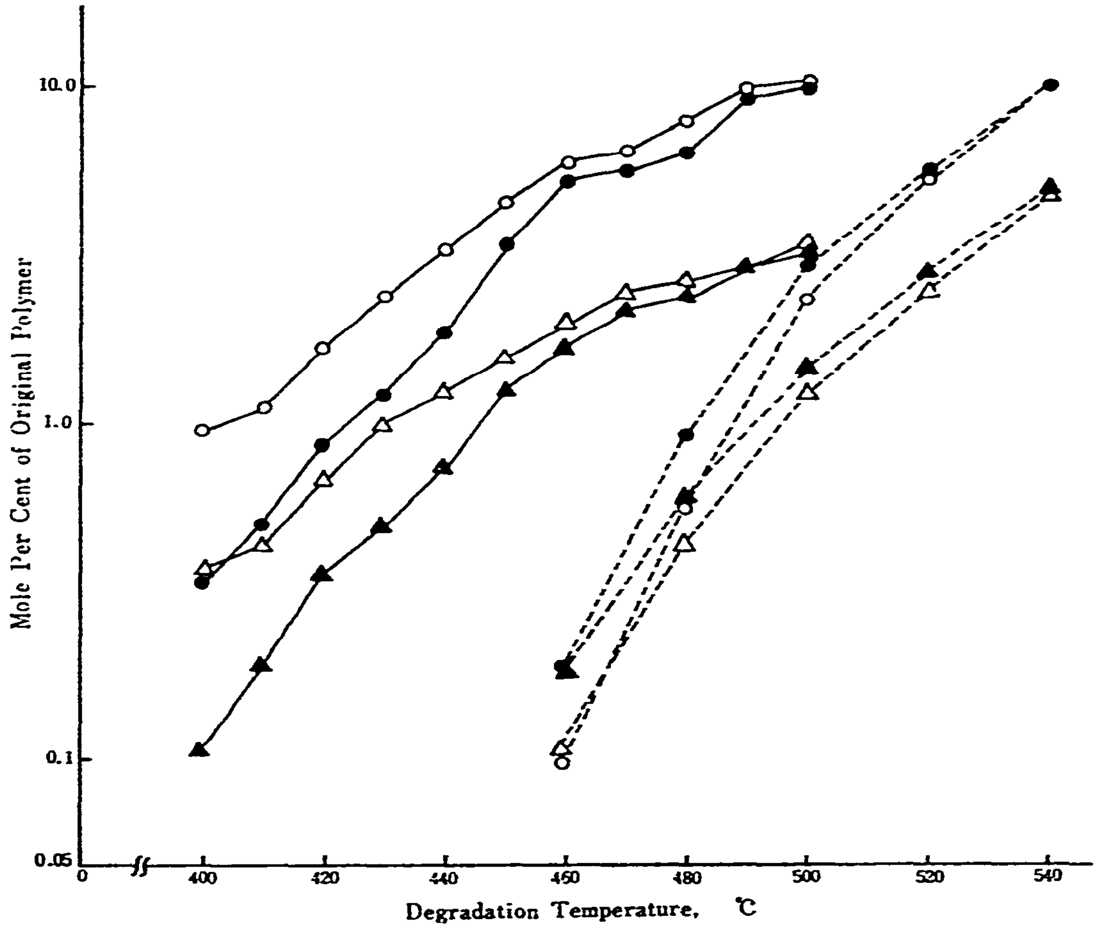

Fig. 10. C_2 and C_3 hydrocarbons produced by the degradation of polyethylenes in air and in nitrogen. Straight line, in air; dotted line, in nitrogen. (○) C_2 for unirradiated low-density polyethylene; (●) C_2 for irradiated low-density polyethylene at 100 Mrad; (△) C_3 for unirradiated low-density polyethylene; (▲) C_3 for irradiated low-density polyethylene at 100 Mrad.

Ethylene is also the most abundant volatile degradation product in air. This may be because the chain scission of polymer molecules occurs easily in the presence of oxygen over this temperature range, and a good deal of volatile monomer radicals and polymer radicals of low molecular weight is produced apart from peroxy radicals.

At low degradation temperatures the quantities of hydrocarbons produced for the irradiated polymer are small compared to those produced for the unirradiated polymer. This is because CO and CO_2 are produced abundantly at the beginning of the oxidative thermal degradation. From the standpoint of the ignition process, it can be said that the irradiated polyethylene is less flammable than the unirradiated polyethylene.

Except for carbonyl compounds no oxidized organic compounds were observed in the oxidative degradation. These carbonyl compounds are produced from the decomposition of hydroperoxides. Alcohols may not be isolated because alcoholic groups react rapidly with oxygen to yield carbonyl-containing compounds. Acid is one of the important products in the autoxidation degradation products. Acids, however, are scarcely evolved in the short degradation period at temperatures of the combustion region.

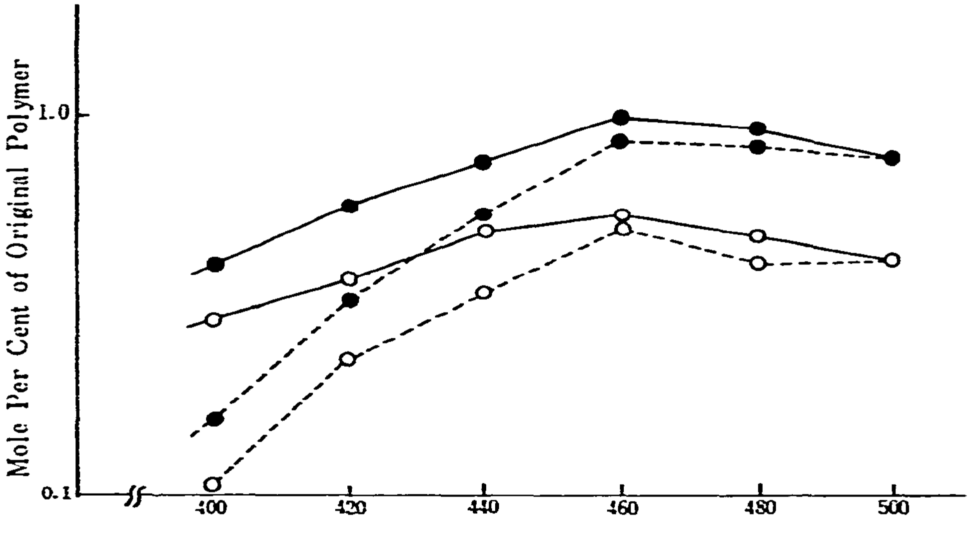

Fig. 11. Aldehydes produced by the oxidative degradation of polyethylenes in air. Straight line, unirradiated polyethylene; dotted line, irradiated polyethylene at 100 Mrad. (○) Acetaldehyde; (●) acrolein and propionaldehyde.

The amount of the degradation products acetaldehyde, acrolein and propionaldehyde is shown in Fig. 11 with varying degradation temperatures. As can be seen the production of these aldehydes does not increase over 460 °C. The ignition temperatures of aldehydes are relatively low, so that the presence of aldehydes in the evolved degradation products may lead to the ignition of polyethylene.

In this investigation, the isothermal degradation method was applied to the oxidative degradation of the polyethylenes. The disadvantage of this procedure is the time required to heat the sample to operating temperature. This disadvantage, however, can be largely overcome by using a small sample cell containing small samples. It might be necessary to consider the catalytic influence of an aluminum cell on the oxidative degradation reaction.

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