

## THE THERMAL STABILITY OF IRRADIATED POLYETHYLENE

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### SUMMARY

Vicat softening-point determination, differential thermal analysis and thermogravimetric analysis were used to investigate the thermal stability of polyethylenes irradiated with electron beams up to 100 Mrad. The softening temperatures of the irradiated low-density polyethylenes increased much more with increase in radiation dose than those of the irradiated high-density polyethylenes. The results of thermogravimetry show that the irradiated polyethylenes decompose in three stages in air, but in one stage in a nitrogen atmosphere. Those irradiated polyethylenes which decompose easily in nitrogen, as shown by calculation of activation energies, begin to decompose at relatively low temperature in air with increasing radiation dose. The irradiated polyethylenes, however, are less combustible than the unirradiated polyethylenes, since the initiation temperature for the second-stage degradation, which probably shows an ignition point, and the residue after the degradation, increase with increase of radiation dose. In addition, the differential thermal analysis was carried out to investigate the mechanism of the thermal decomposition of the irradiated polyethylenes.

### INTRODUCTION

Recently, irradiated polyethylene began to be used widely in industry as cables, films, etc., instead of ordinary polyethylene. It is worthwhile studying the thermal stability (*e.g.* inflammability) of irradiated polyethylene.

A little work has been done on the thermogravimetry of polyethylene cross-linked by irradiation. Wall *et al.*<sup>1</sup> concluded that crosslinking had little effect on the rate of thermal decomposition of polyethylene irradiated with  $\gamma$ -rays as compared with linear polymethylene. Igarashi *et al.*<sup>2</sup> carried out the thermal degradation in nitrogen and in air of high-density polyethylene irradiated with  $\gamma$ -rays, and they found that the thermal stability decreased with increasing radiation dose; but they did not refer to the differential thermal analysis and the combustion of irradiated polyethylene.

The present paper is devoted primarily to a study on the thermal stability of low-density and high-density polyethylene irradiated in air with electron beams up to 100 Mrad, with the measurements of the softening temperature, the decomposition

temperature, the residue after combustion, and the activation energy. The results of the thermogravimetry in air and in nitrogen for the two kinds of irradiated polyethylenes have been compared with the data from the differential thermal analysis.

## EXPERIMENTAL

### *Materials*

The polymers used were low-density polyethylene (highly-branched polyethylene, DFDJ-5505) supplied without additives (Nippon Unicar Co., Tokyo) and high-density polyethylene (scarcely-branched polyethylene, Sholex 6050) supplied with an anti-oxidant content of <0.05% (Japan Olefinc Co., Tokyo). The density and the number-average molecular weight of DFDJ-5505 were reported to be 0.92 and *ca.* 10,000, and those of Sholex 6050 were reported to be 0.96 and *ca.* 10,000.

DFDJ-5505 and Sholex 6050 were moulded at 140°C for about 40 min and at 165°C for about 40 min, respectively, with a vacuum hot-press to get the films of the polymers of about 3-mm thickness.

### *Apparatus*

*Irradiation.* — The moulded samples (60 × 20 × 3 mm) were irradiated in air, at room temperature, with electron beams from a Van de Graaf-type electron accelerator (Tokyo Metropolitan Isotope Research Center). The irradiation conditions were: electron beam current, 10 μA; acceleration energy, 1.5 MeV; electron beam scanner, 32 × 3.5 cm; dose rate,  $1.9 \times 10^4$  rad/sec.

*Softening-temperature determination.* — The apparatus for softening-temperature determination (Vicat softening-point determination apparatus) was constructed according to ASTM designation: D 1525-65T. In this measurement, the heat transfer liquid was silicone oil, and the two heaters had a controller to permit automatic control of the selected rate of temperature rise. The net load on the needle point was 1.020 g.

*Simultaneous measurement of DTA and TG.* — The apparatus for differential thermal analysis (DTA) and thermogravimetry (TG) in this experiment was a commercial thermobalance, Thermoflex type 8021, developed at Rigaku Denki Co., Tokyo.

Sample cells were concentric quartz-glass cylinders. The inside diameter and the depth of the sample cell were 6 mm and 19 mm, respectively. Within the hollow of the internal cylinder, a platinum-platinum/rhodium thermocouple was inserted to measure the temperature difference between the sample and the reference substance. The temperature of the vertical electric furnace was measured by means of a chromel-alumel thermocouple located on the surface of a protective tube for the sample holder of the thermobalance.

### *Experimental procedure*

In the determination of softening temperatures of the polymers, retests were made when the difference between the two specimens was greater than 1°C, and the

softening temperatures were evaluated by taking the average of the two values. The size of a specimen was  $10 \times 5 \times 3$  mm. The heating rate was  $50^\circ\text{C}/\text{h}$ , and the heating started after the hot silicone oil had been cooled down to room temperature by a cooling tube before every run. The distance of the needle penetration was determined by a dial guage, and the softening temperatures were observed by a thermometer.

The irradiated samples were skived to a thickness of about 0.2 mm and kept in a room for more than 3 days before differential thermal analysis and thermogravimetry. The edge of the skived films, which was oxidized during the irradiation in air, was removed before cutting the films into about  $1 \times 1$  mm pieces. The samples, weighing about 32 mg, were placed on the reference substance, calcined alumina, and then the furnace temperature was raised at a constant rate of  $5.6^\circ\text{C}/\text{min}$ , from room temperature to almost  $650^\circ\text{C}$ , in air or nitrogen. Air or nitrogen (purity  $>99.98\%$ ) was introduced from an inlet under the protective tube of the thermobalance, at a flow rate of  $0.7 \text{ l}/\text{min}$ .

By a graphical differentiation of weight-loss curve, the rates of relative weight loss (in  $\%/ \text{min}$ ) were plotted against the temperature for the derivative-thermogravimetry (DTG) curve. The decomposition temperatures were obtained by taking the average of two or three values on the TG curves.

Amounts of gel fraction and crosslinking index were determined by extracting the skived polyethylene films, without removing the oxidized edge, in boiling distilled xylene for 30 h with a 0.1% solution of anti-oxidant, di- $\beta$ -naphthyl-*p*-phenylenediamine.

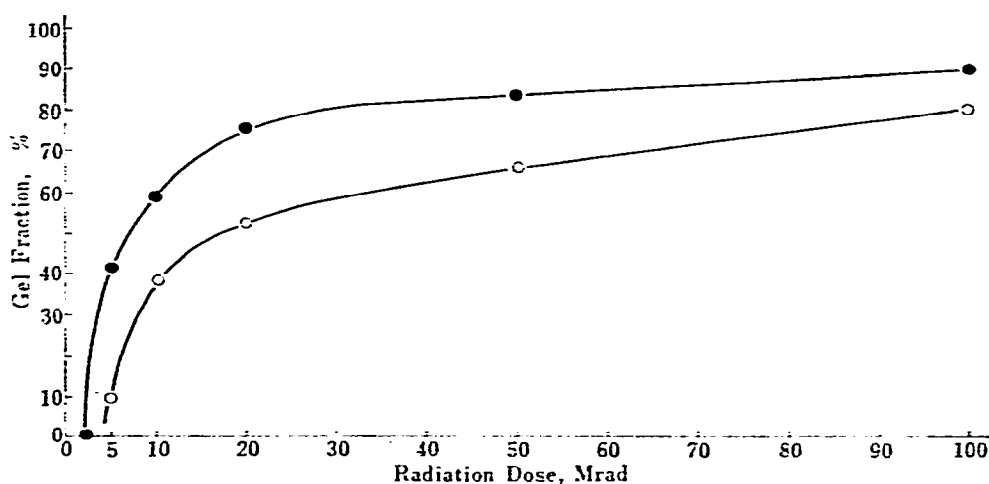


Fig. 1. Variation of gel fraction of polyethylenes with radiation dose: (○) high-density polyethylene; (●) low-density polyethylene.

## RESULTS AND DISCUSSION

### *Measurements of gel fraction and crosslinking index*

The values of gel fraction obtained from the weight losses after the extraction are shown in Fig. 1 and Table I. The results show that the gel fractions of the irra-

**TABLE I**  
**CHANGES IN CROSSLINKING INDEX AND SOFTENING POINT OF**  
**IRRADIATED POLYETHYLENES**

| <i>Sample</i> | <i>Radiation dose (Mrad)</i> | <i>Gel fraction (%)</i> | <i>Crosslinking index</i> | <i>Softening point (°C)</i> |
|---------------|------------------------------|-------------------------|---------------------------|-----------------------------|
| DFDJ-5505     | Unirradiated                 |                         |                           | 93.4                        |
|               | 2                            | 0.5                     | 0.6                       | 96.5                        |
|               | 5                            | 41.5                    | 1.0                       | 98.0                        |
|               | 10                           | 58.8                    | 1.5                       | 98.6                        |
|               | 20                           | 75.1                    | 2.7                       | 99.6                        |
|               | 50                           | 83.4                    | 4.9                       | 101.8                       |
|               | 100                          | 90.1                    | 23.3                      | 108.0                       |
| Sholex 6050   | Unirradiated                 |                         |                           | 127.7                       |
|               | 2                            | 0.1                     | 0.7                       | 129.3                       |
|               | 5                            | 9.3                     | 0.8                       | 129.8                       |
|               | 10                           | 38.3                    | 1.2                       | 130.1                       |
|               | 20                           | 52.1                    | 1.6                       | 129.9                       |
|               | 50                           | 65.8                    | 2.8                       | 132.4                       |
|               | 100                          | 80.4                    | 14.7                      | 133.2                       |

diated polyethylenes increase with increasing radiation dose, and that the irradiated low-density polyethylenes increase in the gel fractions much more than the irradiated high-density polyethylenes.

From the sol fraction  $s$  of the polymer, the crosslinking index  $\gamma$  (number of crosslinked units per number-average primary molecule) is calculated by using the following two equations<sup>3</sup>

$$\gamma = q_0 u_1 R$$

and

$$s + \sqrt{s} = p_0/q_0 + 1/q_0 u_1 R$$

where  $q_0$  and  $p_0$  are constants relating to crosslinking and scission of the chain molecule,  $u_1$  is the number of units in the number-average primary molecule, and  $R$  is the radiation dose. The value of  $p_0/q_0$  is equal to the ratio of degradation and crosslinking probability.

The values of  $p_0/q_0$  for DFDJ-5505 and Sholex 6050 were 0.37 and 0.57, respectively. The values of crosslinking index are also listed in Table I. It is expected that low-density polyethylene crosslinks more easily than high-density polyethylene, and that there is little difference in gel fraction between thick polyethylene film irradiated in air and thin polyethylene film irradiated in the absence of oxygen<sup>4</sup>.

#### *Determination of softening temperature*

The variation of softening temperatures for the irradiated polyethylenes are shown in Figs. 2 and 3 as a function of radiation dose. The softening temperatures for the polymers increase with radiation dose, and the softening temperature of the

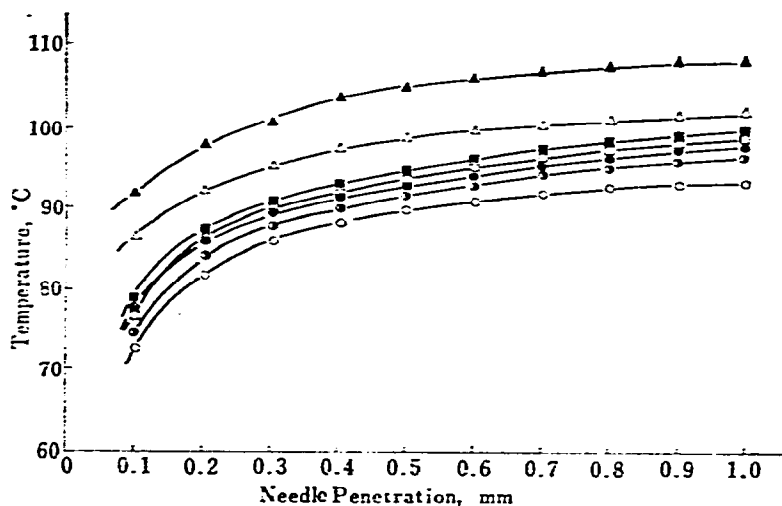


Fig. 2. Softening curves of irradiated low-density polyethylenes by the Vicat method: (○) unirradiated; (◐) at 2 Mrad; (●) at 5 Mrad; (◑) at 10 Mrad; (■) at 20 Mrad; (△) at 50 Mrad; (▲) at 100 Mrad.

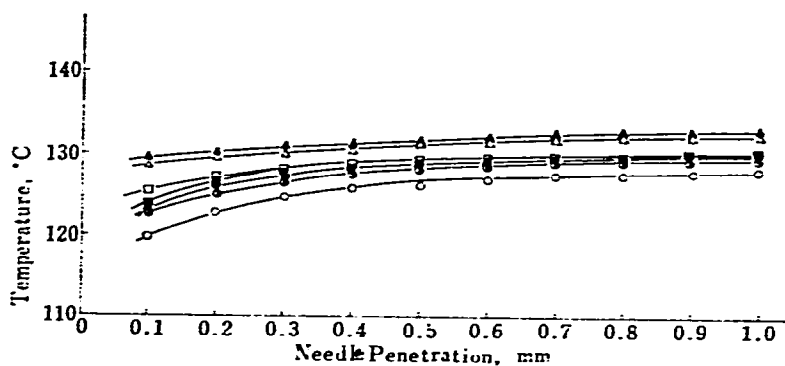


Fig. 3. Softening curves of irradiated high-density polyethylenes by the Vicat method: (○) unirradiated; (◐) at 2 Mrad; (●) at 5 Mrad; (◑) at 10 Mrad; (■) at 20 Mrad; (△) at 50 Mrad; (▲) at 100 Mrad.

low-density polyethylene is influenced much more by irradiation than that of the high-density polyethylene. The softening temperatures for the low-density polyethylenes irradiated at  $> 50$  Mrad are observed to increase rapidly, since the irradiation effects greatly increase three dimensional network structure in the amorphous region of the polymer. On the other hand, the softening temperatures for the irradiated high-density polyethylenes are not changed as much; these temperatures are restricted to about  $120\text{--}130^\circ\text{C}$ , while the needle penetrates a specimen to a depth of  $0.1\text{--}1.0$  mm.

The softening point, the temperature at which the needle penetrates a specimen to a depth of  $1.0$  mm, is plotted against radiation dose in Fig. 4. The increase in softening point of the irradiated low-density polyethylenes is greater than that of the irradiated high-density polyethylenes, for example, the difference of the

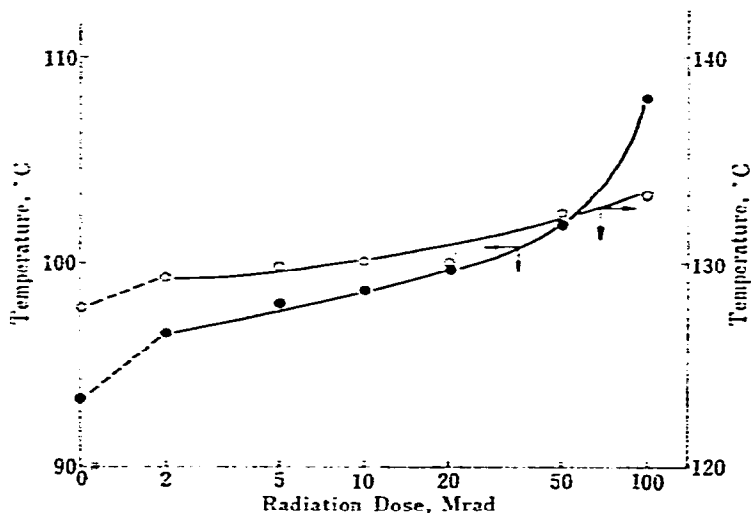


Fig. 4. Variation of the Vicat softening points of irradiated polyethylenes: (○) high-density polyethylene; (●) low-density polyethylene.

softening points between unirradiated and irradiated DFDJ-5505 at 100 Mrad is 14.6°C, while this difference for Sholex 6050 is only 5.5°C.

Softening temperature has a close relationship with thermal stability of high polymers. The more the internal rotations around carbon-carbon bonds in a molecular chain are sterically hindered, the less bent is the molecular chain, and then the softening temperature for the polymer will be increased<sup>5</sup>. It is clear that the irradiated polyethylenes have difficulty in rotating internally because of three dimensional network structure produced by the irradiation. This is the main reason why the highly-crosslinked polyethylenes have the high softening temperatures.

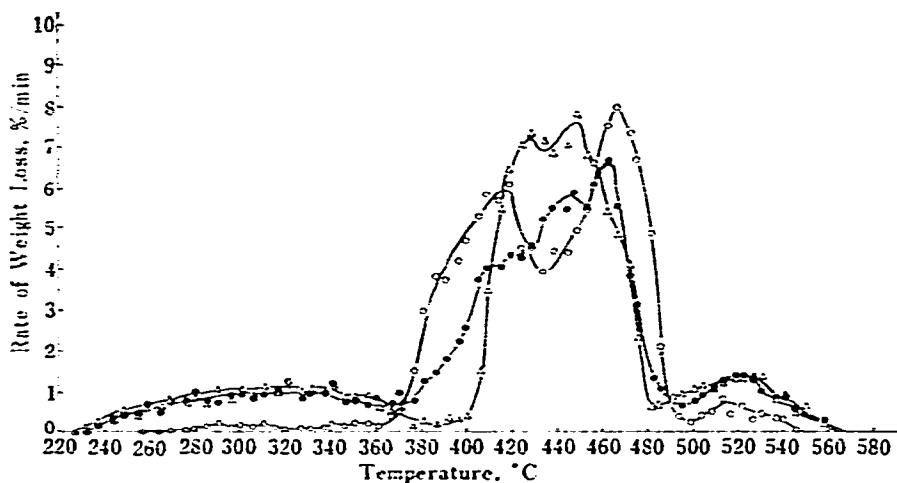


Fig. 5. DTG curves of irradiated low-density polyethylenes in air: (○) unirradiated; (●) at 20 Mrad; (△) at 100 Mrad.

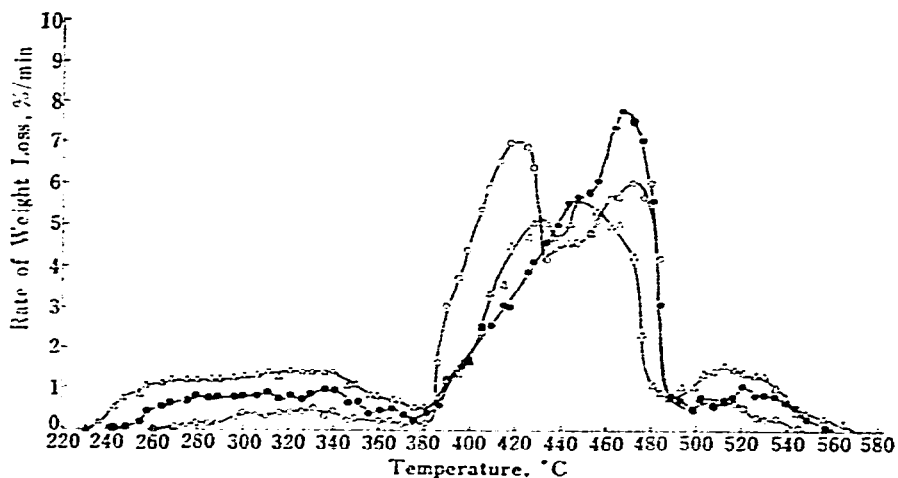


Fig. 6. DTG curves of irradiated high-density polyethylenes in air: (O) unirradiated; (●) at 20 Mrad; (△) at 100 Mrad.

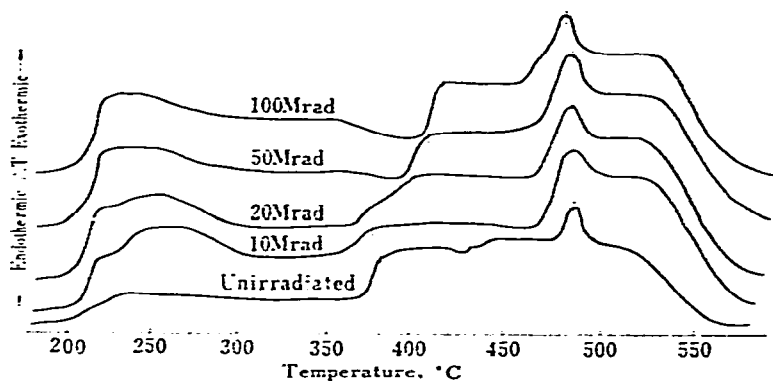


Fig. 7. DTA curves of irradiated low-density polyethylenes in air.

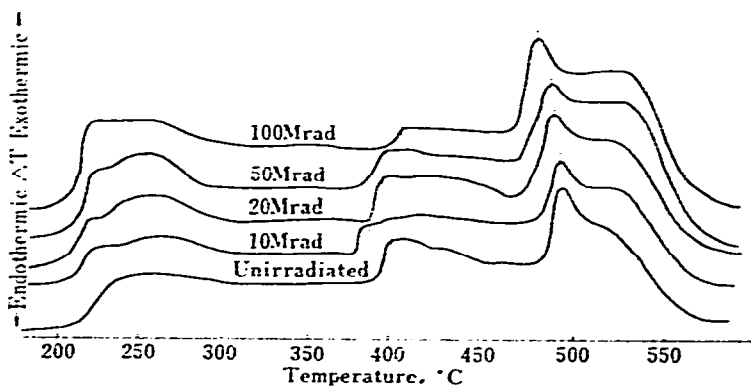


Fig. 8. DTA curves of irradiated high-density polyethylenes in air.

### DTA and TG in air

Simultaneous measurement of DTA and TG was carried out to study the thermal decomposition of the irradiated polymers in air.

The DTG curves for the low-density polyethylenes and the high-density polyethylenes irradiated at 20 Mrad and 100 Mrad are shown in Figs. 5 and 6, respectively, in comparison with the unirradiated polyethylenes. These figures show some differences when compared with the results of Igarashi *et al.*<sup>6</sup>. Figs. 7 and 8 show the DTA curves for the two kinds of polyethylenes. The results from the DTG curves are summarized in Table II.

In air the unirradiated and the irradiated polyethylenes decompose clearly in three stages, as shown in the DTG curves, and this is also observed in the DTA curves with three exothermic peaks corresponding to each degradation stage.

TABLE II  
THERMOGRAVIMETRY RESULTS OF IRRADIATED POLYETHYLENES IN AIR

| Sample      | Radiation dose (Mrad) | Initial temp.              | Initial temp.              | Final temp.      | Weight loss (%) |           | Residue (%) |
|-------------|-----------------------|----------------------------|----------------------------|------------------|-----------------|-----------|-------------|
|             |                       | for 1st stage decomp. (°C) | for 2nd stage decomp. (°C) | for decomp. (°C) | 1st stage       | 3rd stage |             |
| DFDJ-5505   | Unirradiated          | 254                        | 373                        | 554              | 2.9             | 3.9       | 0           |
|             | 5                     | 242                        | 375                        | 557              | 12.9            | 10.0      | 0           |
|             | 10                    | 239                        | 376                        | 559              | 16.2            | 12.0      | 0           |
|             | 20                    | 232                        | 390                        | 563              | 19.4            | 13.2      | 0           |
|             | 50                    | 230                        | 400                        | 559              | 17.6            | 12.4      | 0           |
|             | 100                   | 228                        | 408                        | 561              | 18.2            | 13.0      | 0           |
| Sholex 6050 | Unirradiated          | 261                        | 393                        | 537              | 5.6             | 5.0       | 0           |
|             | 5                     | 259                        | 388                        | 545              | 5.2             | 5.1       | 0           |
|             | 10                    | 248                        | 387                        | 552              | 11.0            | 8.1       | 0           |
|             | 20                    | 242                        | 390                        | 560              | 14.5            | 9.9       | 0           |
|             | 50                    | 236                        | 397                        | 563              | 21.9            | 12.7      | 0           |
|             | 100                   | 231                        | 400                        | 567              | 25.8            | 15.1      | 0           |

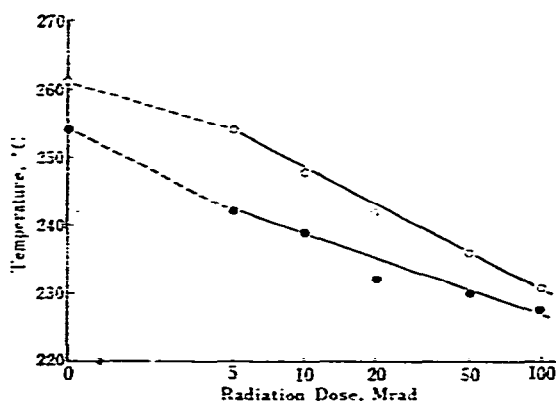


Fig. 9. Variation of initiation temperatures for the first-stage degradation of irradiated polyethylenes in air: (○) high-density polyethylene; (●) low-density polyethylene.



The initiation temperatures for the thermal decomposition of the irradiated specimens are decreased with increase of radiation dose, as shown in Fig. 9. Fig. 10 shows that the quantities of evolved gas from the irradiated high-density polyethylenes are proportional to radiation dose in the first stage degradation. But this quantity seems to reach a maximum at around 20 Mrad for the irradiated low-density polyethylenes, as shown in Fig. 11.

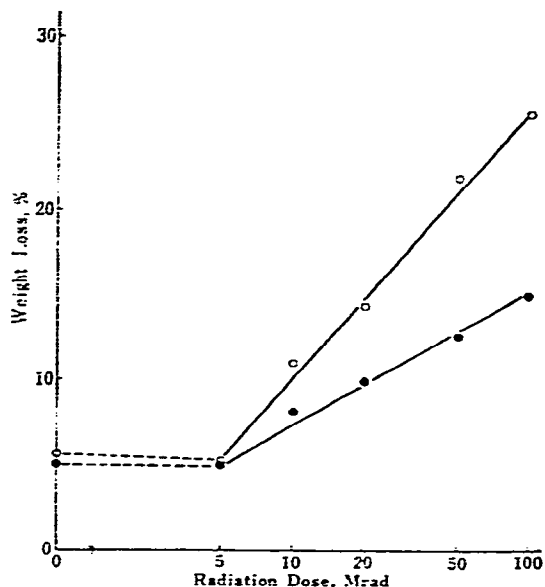


Fig. 10. Variation of weight losses at each stage of degradation for irradiated high-density polyethylenes in air: (○) first stage; (●) third stage.

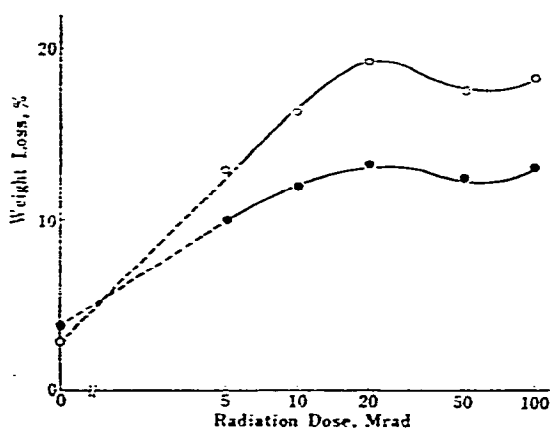


Fig. 11. Variation of weight losses at each stage of degradation for irradiated low-density polyethylenes in air: (○) first stage; (●) third stage.

The first stage degradation is expected to be a slow thermal oxidation with evolution of oxides. The author has confirmed, by gas chromatography, that signifi-

cant quantities of carbon dioxide are produced from the irradiated specimens when decomposed in air at 320°C, and that the high-density polyethylene irradiated at 100 Mrad produces much more carbon dioxide than the low density polyethylene irradiated with the same radiation dose.

The case of oxidation for irradiated polyethylene is reported to increase with the larger number of tertiary carbon atoms resulting from crosslinking, and by the presence of vinylene unsaturation<sup>7</sup>. The increase of the oxidation with radiation dose is observed for the irradiated high-density polyethylenes in the first stage degradation; but for the irradiated low-density polyethylenes, the quantities of evolved gas in the first stage degradation are not increased at a radiation dose over 20 Mrad. This may be due to the fracture of branched chains of the polymer by the irradiation with a high radiation dose. Therefore, the quantities of degradation products of the low-density polyethylenes irradiated at over 50 Mrad decrease as compared with those of the high-density polyethylenes irradiated with the same radiation dose.

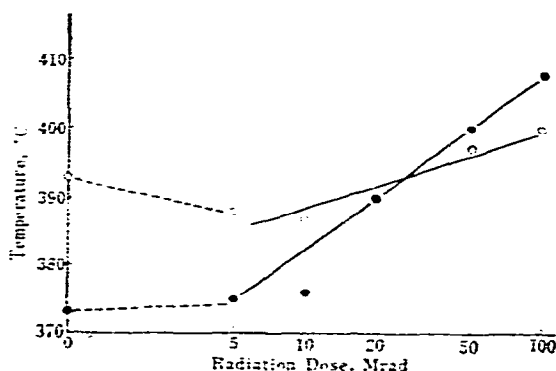


Fig. 12. Variation of initiation temperatures for the second-stage degradation of irradiated polyethylenes in air: (○) high-density polyethylene; (●) low-density polyethylene.

As shown in Fig. 12, the initiation temperatures for the second stage degradation, which are presumably ignition points, are increased with increase in radiation dose for the irradiated low-density polyethylenes, but not increased for the irradiated high-density polyethylenes, at a relatively low radiation dose. This tendency to increase the ignition points is clearly due to three dimensional network formation in the irradiated polymers. It is expected, from the figure, that the ignition points of the low-density polyethylenes are higher than those of the high-density polyethylenes when irradiated at over 50 Mrad.

The mechanisms of the oxidative degradation in the second stage differ with different radiation doses (see Figs. 5 and 6). Both unirradiated polyethylenes decompose in two stages, but the irradiated polyethylenes have a tendency to decompose in one stage as the radiation dose is increased. However, it is not clear whether these decompositions are caused by oxidative degradation, depolymerization, or random degradation of oxidized products.

The temperature at which the second-stage degradation terminates is about 500°C for all the specimens, and this corresponds to the termination temperature for the thermal decomposition in a nitrogen atmosphere. In the presence of air, however, a certain amount of residue remains at a temperature over 500°C, and the third stage degradation continues up to 550–580°C with the slow thermal oxidation of the residue. The residue is probably carbonized products, due mostly to crosslinking formed by the irradiation process.

The amount of residue left after the second stage degradation, for the irradiated high-density polyethylenes, increases proportionally with radiation dose, but it seems not to increase with doses over 20 Mrad for the irradiated low-density polyethylenes (see Figs. 10 and 11). The reason why the quantities of the residue are not increased with increasing radiation dose for the irradiated low-density polyethylenes is probably due to the increase of vinylene unsaturation, or the remaining of tertiary carbon atoms after the irradiation.

Maintenance of combustion is dependent on the quantity of residue left after the combustion. The irradiated high-density polymers, therefore, tend to become slightly combustible with increasing radiation dose, but the combustibility would not seem to be affected by the radiation dose for the low-density polymers, irradiated at over 20 Mrad.

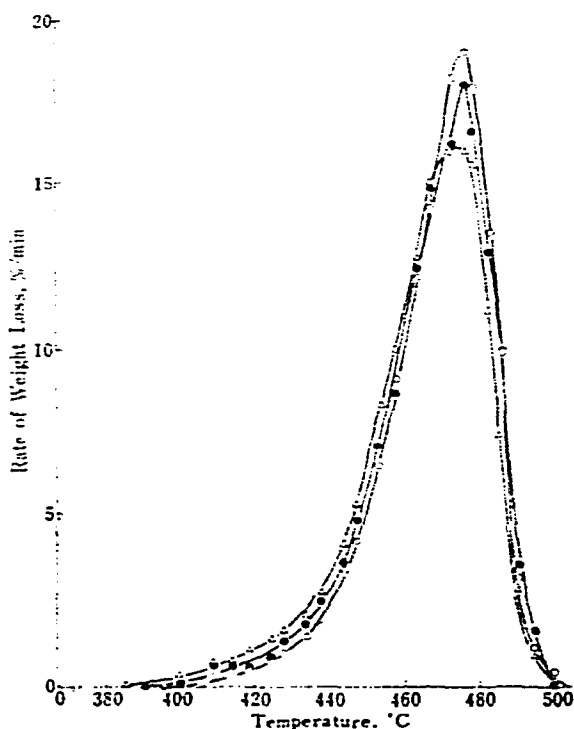


Fig. 13. DTG curves of irradiated low-density polyethylenes in a nitrogen atmosphere; (○) unirradiated; (●) at 20 Mrad; (△) at 100 Mrad.

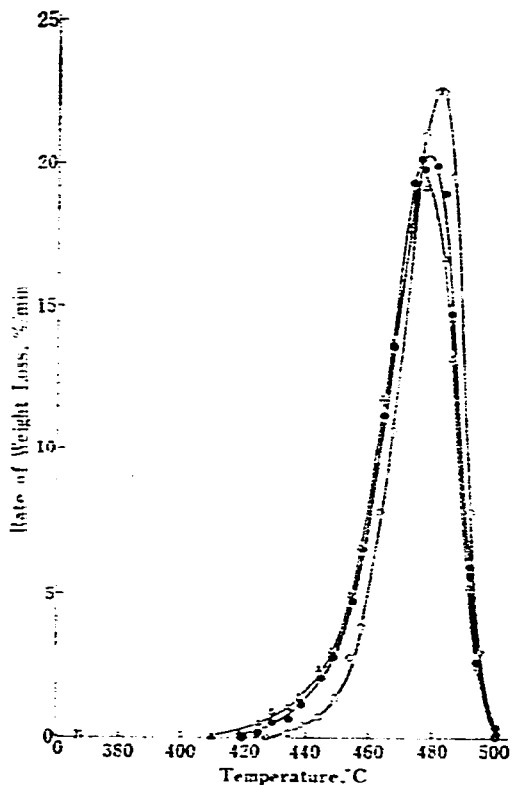


Fig. 14. DTG curves of irradiated high-density polyethylenes in a nitrogen atmosphere: (○) unirradiated; (●) at 20 Mrad; (△) at 100 Mrad.

#### *TG in nitrogen*

Figs. 13 and 14 show the DTG curves in nitrogen for the low-density polyethylenes and the high-density polyethylenes, respectively, irradiated at various doses.

The initiation temperatures for the thermal decomposition in nitrogen of the irradiated specimens also have a tendency to decrease with increase of radiation dose, and the rate of weight loss at a certain temperature increases with increasing radiation dose. On the other hand, the irradiated and unirradiated low-density polyethylenes decompose easier than the high-density polyethylenes at atmospheric pressure.

In order to investigate the thermal stability of the irradiated specimens in nitrogen, the apparent activation energy and the order of reaction were evaluated from the TG curves by the method of Freeman and Carroll<sup>8</sup>. They derived the following equation

$$\Delta \log(dw/dt) / \Delta \log W_r = n - E / 2.3 R \times \Delta(1/T) / \Delta \log W_r$$

where  $dw/dt$  is the rate of change in weight,  $W_r$  is the weight of the reactant at the absolute temperature  $T$ ,  $n$  is the order of reaction,  $E$  is the apparent activation energy, and  $R$  is the gas constant. In Figs. 15 and 16 the linear plots of  $\Delta \log(dw/dt) / \Delta \log W_r$  against  $\Delta(1/T) / \Delta \log W_r$  are shown for the thermal decomposition of the irradiated

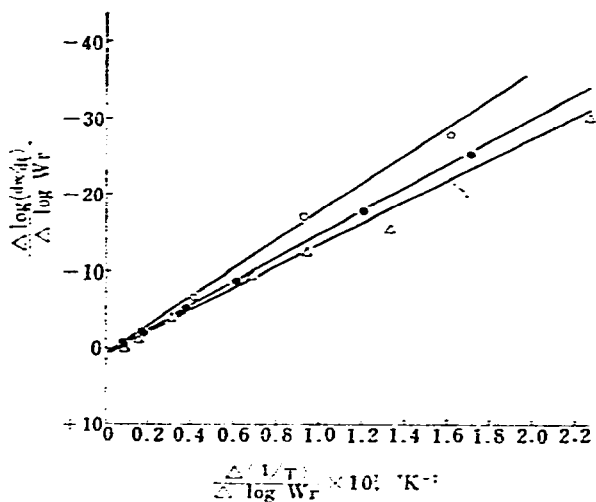


Fig. 15. Freeman's plots for thermal decomposition of irradiated low-density polyethylenes in nitrogen: (○) unirradiated; (●) at 20 Mrad; (△) at 100 Mrad.

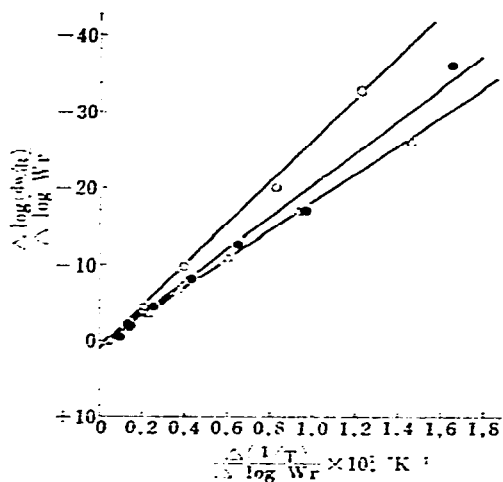


Fig. 16. Freeman's plots for thermal decomposition of irradiated high-density polyethylenes in nitrogen: (○) unirradiated; (●) at 20 Mrad; (△) at 100 Mrad.

TABLE III  
THERMOGRAVIMETRY RESULTS OF IRRADIATED POLYETHYLENES  
IN NITROGEN

| Sample      | Radiation dose (Mrad) | Decomp. temp. (°C) | Activation energy (kcal/mole) | Residue (%) |
|-------------|-----------------------|--------------------|-------------------------------|-------------|
| DFDJ-5505   | Unirradiated          | 396-496            | 84                            | <2          |
|             | 20                    | 390-494            | 69                            | <2          |
|             | 100                   | 385-500            | 64                            | <2          |
| Sholex 6050 | Unirradiated          | 427-499            | 125                           | <2          |
|             | 20                    | 420-497            | 96                            | <2          |
|             | 100                   | 410-496            | 88                            | <2          |

specimens compared to the unirradiated specimens. The activation energies thus obtained are listed in Table III. The order of reaction for these specimens is approximately 1.

The activation energies of the irradiated polyethylenes decrease compared with those of the unirradiated polyethylenes. However, the activation energy of the unirradiated high-density polyethylene (125 kcal/mole) is higher than the value of 73.6 kcal/mole, which was obtained for the low-pressure polyethylene (Hizex 7000) with the same procedure by Igarashi *et al.*<sup>9</sup>. This discrepancy may be caused by the differences in the size of the sample cell and the heating rate.

The thermal instability of the irradiated specimens in nitrogen is mostly assumed to be dependent on the increase of the tertiary carbon atoms and the vinylene unsaturation, but it would also be affected by the presence of carbonyl compounds and hydroperoxides produced with diffused oxygen in the polymers by radio-oxidation.

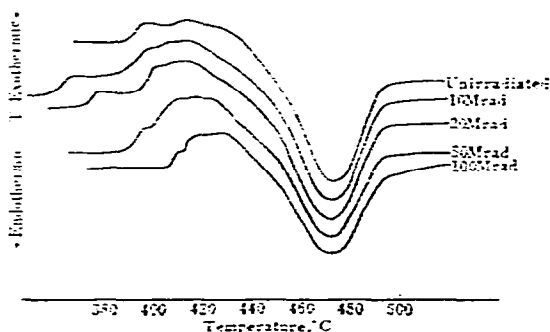


Fig. 17. DTA curves of irradiated low-density polyethylenes in nitrogen.

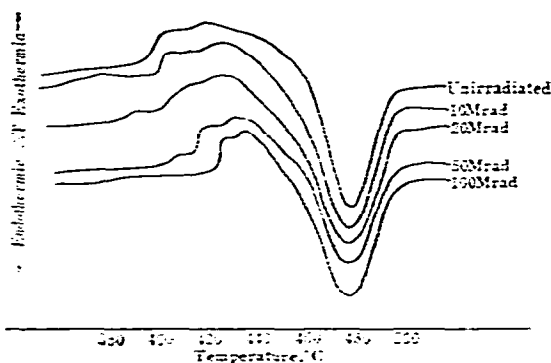


Fig. 18. DTA curves of irradiated high-density polyethylenes in nitrogen.

#### DTA in nitrogen

In the thermal decomposition in a nitrogen atmosphere, the DTA curves for the specimens were obtained at the same time as the TG curves. The DTA curves, which consist of an exothermic peak and an endothermic peak are shown in Figs. 17 and 18.

It is observed from the figures that the exothermic peaks for the irradiated polyethylenes are shifted to a higher temperature as radiation dose is increased. The exothermic energies, which would be expected to be proportional to the exothermic areas, have a tendency to decrease with increase in radiation dose.

It seems to become more difficult to rearrange molecules of the crosslinked polyethylenes with increasing radiation dose, over a certain temperature range, before the thermal decomposition. This effect may be a main reason why the exothermic reaction occurs in a nitrogen atmosphere and the exothermic areas are decreased with increase in radiation dose.

The initiation temperatures for the degradation of the irradiated specimens should increase as radiation dose increases, provided the thermal degradation initiates at the temperature of the exothermic peak. But the result from the thermogravimetry is reversed, namely the weight losses on the TG curves for the irradiated specimens are observed at the temperature of the exothermic peaks on the DTA curves. For example, the low-density polyethylene irradiated at 100 Mrad loses about 5% of its total weight at the peak temperature, whereas the high-density polyethylene loses about 2% when irradiated at the same dose. This phenomenon is presumably responsible for a slow evaporation of degradation products from the relatively large quantity of the sample, and then an endothermic peak will not be observed on the DTA curves.

The endothermic peaks on the DTA curves correspond to the temperatures indicating the maximum weight loss on the TG curves, and the peaks tend to shift to a lower temperature with increase in radiation dose. These results are compatible with the data from the TG curves.

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