

# Effect of Large Dosage Irradiation in Air on Polyethylene

TAKASHI FUJIMURA, NAOHIRO HAYAKAWA, and ISAMU KURIYAMA, *Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Watanuki-machi, Takasaki, Gunma, 370-12, Japan*

## Synopsis

The large dosage irradiation effect on polyethylene in air was examined by the method of double irradiation. Polyethylene was first irradiated with  $\gamma$ -rays to a dosage of a few hundred Mrad in air at 298°K. The formed radicals were destroyed, and the polymer, changed chemically and morphologically, was irradiated again *in vacuo* at 77°K with a dose of 12.7 Mrad. The thermal decay of radicals produced in polyethylene by the second irradiation was investigated. The results were compared with the sample not exposed to the first irradiation. The results were also compared with previous data of polyethylene irradiated *in vacuo* to a great extent and then treated in the same manner as that in the present experiment. The results show that scission of the polymer chain by oxidation makes the radical decay faster. Simultaneously, crosslinks formed in polyethylene irradiated in air to a great extent slow down the radical decay. Almost the same number of double bonds was formed in polyethylene irradiated in air as in polyethylene irradiated *in vacuo*. These double bonds react with alkyl radicals to form allyl radicals.

## INTRODUCTION

In our previous work,<sup>1</sup> the effect of large dosage irradiation *in vacuo* on polyethylene was investigated by the method of double irradiation with electron spin resonance (ESR) spectroscopy. The number of polymeric materials used in radiation fields for long periods has increased rapidly. In many actual cases, polymer materials are irradiated in air instead of *in vacuo*. It is important to know the radiation effect of polymeric materials irradiated in air to a great extent.

Many investigations<sup>2-5</sup> of the effect of small dosage irradiation in air, 1-99 Mrad, on polymers have used ESR. Little is known about effect on polyethylene irradiated with hundreds of megarads in air.

It should be noted that there is a great difference between the polymer matrix before and after a large dosage irradiation in air. After a large dosage irradiation in air, the polymer matrix was changed by degradation and by the formation of double bonds and crosslinks. When the changed polymer is irradiated further, the radicals behave differently in the chemically and morphologically changed polymer matrix.

The aim of the present work is to investigate the characteristics of the radicals in polymer already changed chemically and morphologically by hundreds of megarads irradiation in air. It is important to know the difference of radical behavior before and after a large dosage irradiation in air. To investigate the effect of large dosage irradiation in air on polyethylene, the data of polyethylene irradiated to a large extent in this work in air will be compared with the previous

data<sup>1</sup> of polyethylene irradiated to a large extent *in vacuo*. These results are likely to be useful for simulation of the effect of very large doses in air.

## EXPERIMENTAL

The sample used was high-density polyethylene Sholex 6050 in the form of powder. The samples in air at 298°K were  $\gamma$ -irradiated from a <sup>60</sup>Co source with various large doses at a dose rate of 0.7 Mrad/h. After a large dosage irradiation, the radicals were destroyed by leaving samples in air for long periods. Samples were evacuated and irradiated again *in vacuo* at 77°K with  $\gamma$ -rays up to 12.7 Mrad at a dose rate of 0.7 Mrad/h.

ESR measurements were made at 77°K with a Varian V-4502 X-band spectrometer with 100 kHz field modulation. Heat treatment experiments to study the decay of radicals were carried out in the following way. Samples after the second irradiation at 77°K were heated to fixed temperatures for 5 min and cooled back to 77°K for measurements.

## RESULTS

High-density polyethylene in the form of powder was irradiated in air at 298°K with a dose of 260 Mrad. This irradiation is referred to as the "first irradiation." After irradiation, the resulting radicals were destroyed by leaving samples in air for long periods. The sample was evacuated and irradiated again *in vacuo* at 77°K with a dose of 12.7 Mrad. This second irradiation is called the "second irradiation." This sample is described as "sample 1."

The ESR spectrum of sample 1 treated as above was obtained at 77°K (see Fig. 1). The sextet spectrum, the average hyperfine splitting of which is 32G, is assigned to alkyl radicals.

When sample 1 was heated and cooled back to 77°K for examination, the spectrum was observed to vary both in shape and intensity. The variation of relative intensity with heating temperature is shown in Figure 2.

This figure refers to three samples. The first is "sample 1." The second sample is different in only the dosage of the first irradiation, 100 instead of 260 Mrad; this is "sample 2." High-density polyethylene in the form of powder was irradiated *in vacuo* at 77°K with a dose of 12.7 Mrad, and ESR spectrum was observed at 77°K; this "sample 3" underwent the second irradiation only. The number of radicals produced in the second irradiation at 77°K was the same in the three samples.

For comparison, the variation of relative intensity of following sample is indicated by dotted line in Figure 2. High-density polyethylene in the form of powder was irradiated *in vacuo*<sup>1</sup> at 298°K with a dose of 400 Mrad. After irradiation, the resulting radicals were destroyed by introducing air. The sample was evacuated again and irradiated again *in vacuo* at 77°K with a dose of 12.7 Mrad.

Three-step decay<sup>6-8</sup> of radicals produced in polyethylene irradiated *in vacuo* with a dose of around 15 Mrad at 77°K has been reported, and three decay regions of radicals are observed in Figure 2. For sample 3, the first and second decay regions are around 120°K and 200°K, respectively, and the third above 250°K. Recently, it has been found that some of the alkyl radicals detected at 77°K are

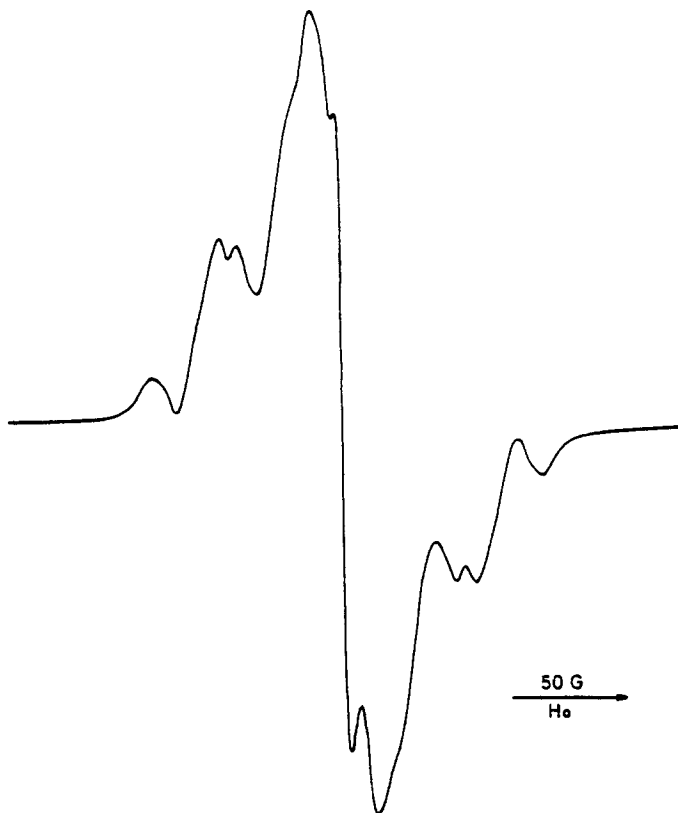


Fig. 1. ESR spectrum obtained with the sample treated as following. High-density polyethylene in the form of powder was at first irradiated in air at 298°K with a dose of 260 Mrad (sample 1). After the first irradiation, radicals formed were abolished by leaving the sample in air for a long period. Sample was evacuated again and irradiated for a second time *in vacuo* at 77°K with a dose of 12.7 Mrad. ESR measurement was carried out at 77°K.

trapped very close to each other in polyethylene matrix, forming radical pairs.<sup>9,10</sup> The first decay region was ascribed to the decay of these pairs.<sup>6</sup> The second decay region was connected with radicals trapped in the noncrystalline regions.<sup>6</sup> The third decay region was correlated with radicals trapped in the crystalline regions.<sup>6</sup>

The main difference in the decay curves in Figure 2 among samples 1, 2, and 3 are between 150°K and 200°K and between 240°K and 300°K. The decay amounts are large between 150°K and 200°K when the samples are irradiated in air to a great extent. In this temperature range, the decay amount of samples 1 and 2 irradiated in air to a large extent was larger than those of sample irradiated *in vacuo* to a great extent (dotted line in Fig. 2). These result suggests that these differences in the decay curve are the effect of oxygen.

Between 240°K and 300°K, the decay amount decreases when the dose of large dosage irradiation in air increases. In this temperature range, the decay amount of sample 1 irradiated in air with a dose of 260 Mrad is larger than that of sample irradiated *in vacuo* (dotted line in Fig. 2).

Above 300°K, there are no difference between samples 1, 2, and 3. In this temperature range, the decay amount of sample 1 is smaller than that of sample irradiated *in vacuo* with a dose of 400 Mrad (dotted line in Fig. 2).

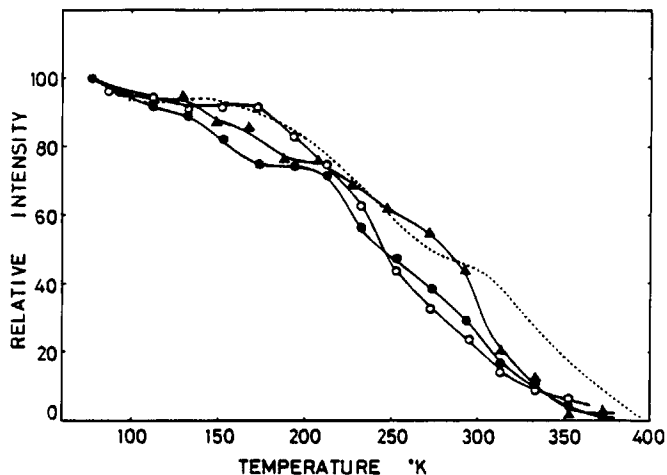


Fig. 2. Thermal decay curves of radicals produced by the second irradiation of 12.7 Mrad *in vacuo* at 77°K for following four samples: (●) high-density polyethylene in the form of powder was at first irradiated in air with a dose of 260 Mrad (sample 1); (▲) the same original sample having undergone the first irradiation in air of 100 Mrad (sample 2); (○) the same original sample without first irradiation (sample 3); (---) the same original sample having undergone the first irradiation *in vacuo* of 400 Mrad. After the first irradiation, radicals produced in samples 1 and 2 were abolished. Samples 1, 2, and 3 were evacuated again and irradiated for a second time up to 12.7 Mrad *in vacuo* at 77°K. These four samples, having undergone a second irradiation at 77°K, were heated to a fixed temperature for 5 min and cooled to 77°K for ESR measurements.

In order to clarify these differences in total radical decay, the following analysis was carried out.

When sample 1 was heated to 353°K and cooled back to 77°K, the observed spectrum changed as shown in Figure 3. This septet spectrum is attributed to allyl radicals. A small amount of asymmetrical spectrum is superimposed on the center part of the spectrum of allyl radicals. This asymmetrical spectrum

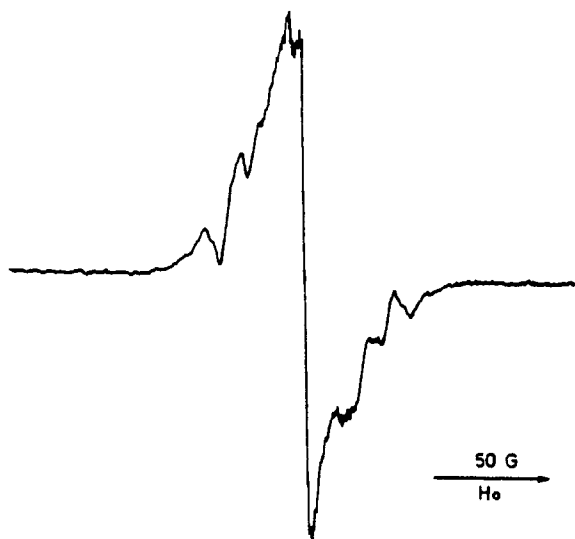


Fig. 3. "Sample 1" treated as described in the caption of Figure 1 was heated to 353°K for 5 min and cooled back to 77°K. ESR measurements was carried out at 77°K.

is due to peroxy radicals. Figure 4 illustrates the conversion of alkyl radicals to allyl radicals<sup>11</sup> for sample 1. The number of allyl radicals is calculated by subtracting the intensity of alkyl radicals from that of total radicals. Allyl radicals appear around 230°K and increase in number to 270°K but decrease on annealing at higher temperature with the decrease of the total radicals. The increase of allyl radicals is accompanied by rapid decrease in the number of alkyl radicals. In Figure 5, the formation and decay of allyl radicals are compared for samples 1, 2, and 3. The peak values around 270°K in samples 1 and 2 are larger than that of sample 3. Above 300°K, however, there are no difference on decay curve between samples 1, 2, and 3.

The peak value of sample 1 is almost same as that of sample irradiated *in vacuo* with a dose of 400 Mrad, shown in Figure 5 by dotted line. It should be noted that the decay curve of sample 1 is shifted to lower temperature than that of sample irradiated *in vacuo*.

Figure 6 shows the decay curve of alkyl radical. Between 250°K and 300°K, the decay curve of sample 1 shifted to higher temperature than that of sample 3. Above 300°K, there is no difference on decay curve between samples 1 and 3.

Below 300°K there is no difference on decay curve between sample 1 irradiated in air and sample irradiated *in vacuo* with a dose of 400 Mrad, shown by dotted line in Figure 6. Above 300°K, the decay curve of sample 1 is shifted to lower temperature than that of sample irradiated *in vacuo*.

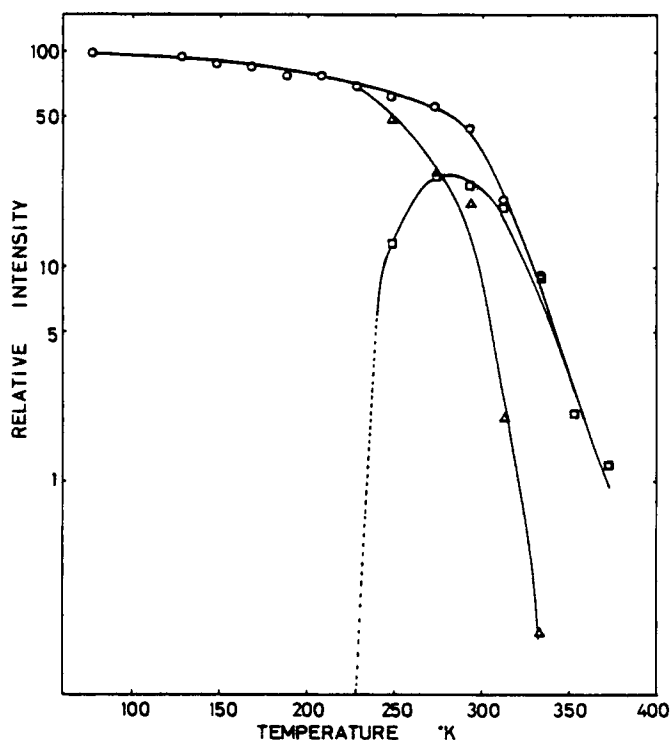


Fig. 4. Conversion of alkyl radicals to allyl radicals in the sample treated as in the caption of Figure 2. Irradiation was carried out in air with a dose of 260 Mrad (sample 1): (O) total radical; (Δ) alkyl radical; (□) allyl radical.

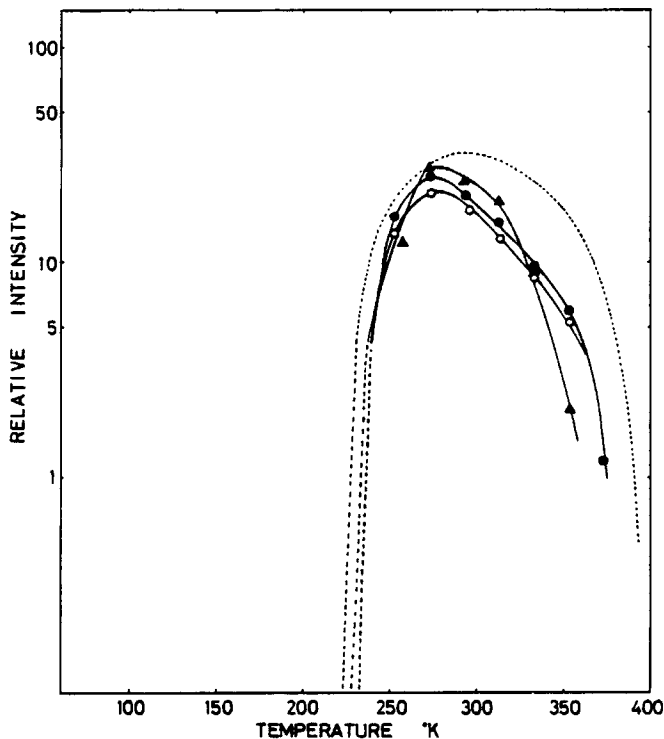


Fig. 5. The formation and decay of allyl radicals in the samples treated as described in the caption of Figure 2. First irradiation dosage and atmosphere: (●) 260 Mrad in air (sample 1); (▲) 100 Mrad in air (sample 2); (○) 0 Mrad (sample 3); (- - -) 400 Mrad *in vacuo*.

## DISCUSSION

As shown in Figure 5, allyl radicals appear above 200°K. Below 200°K only alkyl radicals are produced. As shown in Figure 2, the main difference between the decay curve of alkyl radicals in samples 1 and 2 irradiated in air to a great extent and that of the sample irradiated *in vacuo* with a dose of 400 Mrad (dotted line) is between 150°K and 200°K. The decay amount in samples 1 and 2 irradiated in air is larger than that in the sample irradiated *in vacuo*. In this temperature range, the decay amount in the sample irradiated in air is also larger than that in sample 3 not exposed to a large dose.

This decay region has been named the second decay region and correlated to radicals trapped in the noncrystalline regions.<sup>5</sup> The large decay amount of samples 1 and 2 in this decay region implies that molecular motion in noncrystalline region of samples 1 and 2 irradiated in air to a great extent became easier than that of sample suffered large dosage irradiated *in vacuo*. Also, this large decay amount of samples 1 and 2 means that molecular motion in noncrystalline region of samples 1 and 2 became easier than that of sample 3 not exposed to a large dose.

The reason for this easier molecular motion can be considered as following. Among a few radiation effects, only chain scission can make molecular motion easier. These difference between samples irradiated in air and *in vacuo* is obviously due to the effect of oxygen. This consideration leads to the conclusion that the scission of polyethylene chain by oxidation is the main cause of these difference in decay curves.

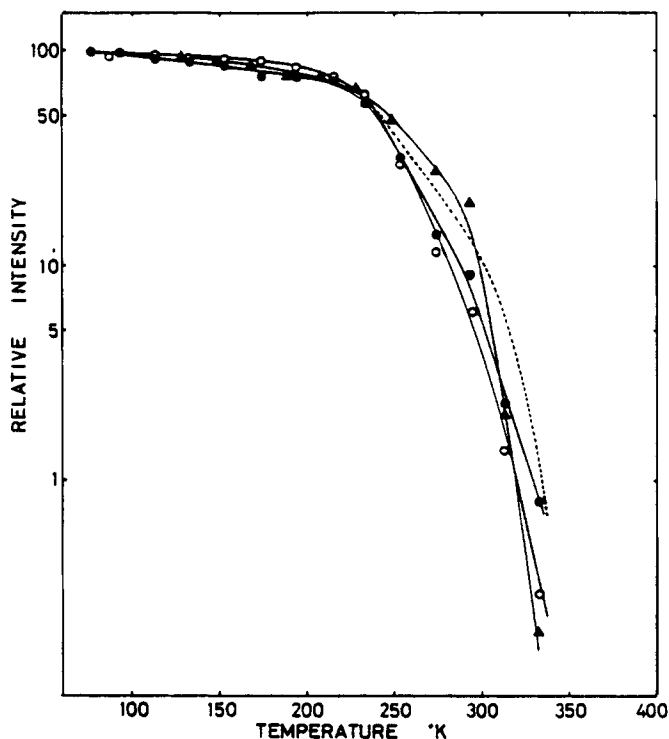


Fig. 6. Thermal decay curve of alkyl radicals only, in the sample treated as described in the caption of Figure 2. The dosage of first irradiation and atmosphere: (●) 260 Mrad in air (sample 1); (▲) 100 Mrad in air (sample 2); (○) 0 Mrad (sample 3); (---) 400 Mrad *in vacuo*.

As shown in Figure 6, between 250°K and 300°K, the decay curve of alkyl radicals in samples 1 and 2 irradiated in air to a great extent was shifted to a higher temperature than in sample 3 not exposed to a large dose. In this temperature range, the decay rate of alkyl radicals in samples 1 and 2 irradiated in air was almost the same as that in the sample irradiated *in vacuo* to a great extent.

As previously reported,<sup>1</sup> in the sample irradiated *in vacuo* to a great extent, the decay curve of alkyl radicals shifted to a higher temperature than that in the sample not exposed to a large dose. Above 250°K, the amount of shift to higher temperature increased as the dosage increased. This shift was attributed to the increase of rigidity in the polymer matrix by crosslinked networks produced by large dosage irradiation *in vacuo*. By the comparison of the shift of decay curve in the sample irradiated in air (samples 1 and 2) and *in vacuo* (dotted line in Fig. 6), crosslinks are suggested to be also produced by large dosage irradiation in air.

Above 300°K, the decay curve of alkyl radicals was shifted to a lower temperature in samples 1 and 2 than in the sample irradiated *in vacuo*. In this temperature range, the decay rate of radicals in samples 1 and 2 was almost the same as that in sample 3 not exposed to a large dose. These results suggest that scission of chain and crosslink reaction occur simultaneously in the sample irradiated in air to a great extent. The crosslinked networks make the decay curve shift to a higher temperature, and the chain scission makes the decay curve shift

to a lower temperature. In the sample irradiated in air, the effects of crosslinks and chain scission on the decay curves cancel each other.

As shown in Figure 5, the peak value of allyl radicals produced in sample 1 irradiated in air with a dose of 260 Mrad is almost same as that in sample irradiated with a dose of 400 Mrad *in vacuo* (dotted line). It has been established that allyl radicals are formed by the reaction of double bonds and alkyl radicals. These results indicate that the amount of double bonds produced in the sample irradiated to a great extent in air is almost same as that in the sample irradiated to the same extent *in vacuo*. Matsuo and Dole<sup>2</sup> also reported no effect of oxygen on the growth of unsaturation during in-source irradiations of polyethylene with rather low ambient oxygen pressures. However, their sample was in the form of films, where oxygen diffusion is not so easy. It should be noted that present data was obtained with the sample in the form of powder, where oxygen could be easily diffused. Moreover, the irradiation dose in the present work was much larger than that in their experiment. The present study indicates no effect of oxygen on the growth of unsaturation even under the condition of easy diffusion for oxygen and large irradiation dose.

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