Effect of Large Dosage Irradiation *In Vacuo* on Polyethylene

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Synopsis

The effect of large dosage irradiation *in vacuo* on polyethylene was investigated by the method of double irradiation. Polyethylene was first irradiated with γ-rays to a dosage of several hundred Mrad *in vacuo* 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 show that many double bonds are formed in the sample irradiated to several hundred Mrad on the first irradiation. Alkyl radicals produced by the second irradiation react with these double bonds yielded by the first irradiation to form a large number of allyl radicals. These allyl radicals are much more stable than alkyl radicals *in vacuo* at 298°K. In a sample not exposed to the first irradiation, almost all radicals formed by the second irradiation decay to form stable products. Crosslinks formed by a large amount of irradiation make the polyethylene matrix more rigid. This rigidity slows down the radical decay. These results suggest that the rate of radical accumulation in polyethylene irradiated *in vacuo* increases as the dosage increases.

INTRODUCTION

The number of polymeric materials used in radiation fields for long periods, such as the insulator of the cable in a nuclear reactor, has increased rapidly. It is important to know the effect of radiation on materials exposed to a large amount of radiation.

As one of the technique to study radiation effects, it is possible to use electron spin resonance (ESR) spectroscopy to study the formation, behavior, and decay of radicals.

Many investigations of the effect[1-6] of small doses *in vacuo*, one to tens Mrad, on polymers have used ESR. When polyethylene is irradiated to a dosage of several thousand Mrad,[7-9] the observed ESR spectrum becomes a singlet which has been assigned to conjugated polyene radical. Little is known about the effect on polyethylene irradiated with several hundred Mrad *in vacuo*.

It should be noted that there is a great difference between the polymer matrix before and after a large amount of irradiation. After a large dose, the polymer was changed by the formation of crosslinks and double bonds and by degradation. 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 several hundred Mrad irradiation. For the study of radiation effects, the atmosphere such as *in vacuo* or in air is very important. As the first part of a series of study, radiation

effect *in vacuo* will be reported here. The results are likely to be useful for the simulation of the effect of very large doses *in vacuo*.

EXPERIMENTAL

The sample used was high-density polyethylene Sholex 6050 in the form of powder. The samples *in vacuo* at 298°K were γ-irradiated from a ^{60}Co source with various large doses at a dose rate of 0.7 Mrad/h. After a large amount of irradiation, the radicals were destroyed by introducing air into the sample tube. Samples were evacuated and irradiated again *in vacuo* at 77°K with γ-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 AND DISCUSSION

High-density polyethylene in the form of powder was irradiated *in vacuo* at 298°K with a dose of 400 Mrad. This irradiation is refered to as "first irradiation." After irradiation, the resulting radicals were destroyed by introducing air at room temperature. The sample was evacuated again 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 was obtained at 77°K (see Fig. 1). The sextet spectrum, the average hyperfine splitting of which is 32 G, 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 and degree of spectral resolution, denoted S, with heating temperature are shown in Figures 2 and 3.

These figures refer to three samples. The first is "sample 1." The second sample is different only in the dosage of the first irradiation, 638 instead of 400 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 the ESR spectrum was observed at 77°K; this "sample 3" suffered the second irradiation only. The number of radicals produced at 77°K was the same in the three samples.

Three-step decay[5,10,11] 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 trapped very close to each other in polyethylene matrix, forming radical pairs.[2,12] The first decay region was ascribed to the decay of these pairs.[5] The second decay region was connected with radicals trapped in the noncrystalline regions.[5] The third decay region was correlated with radicals trapped in the crystalline regions.[5]

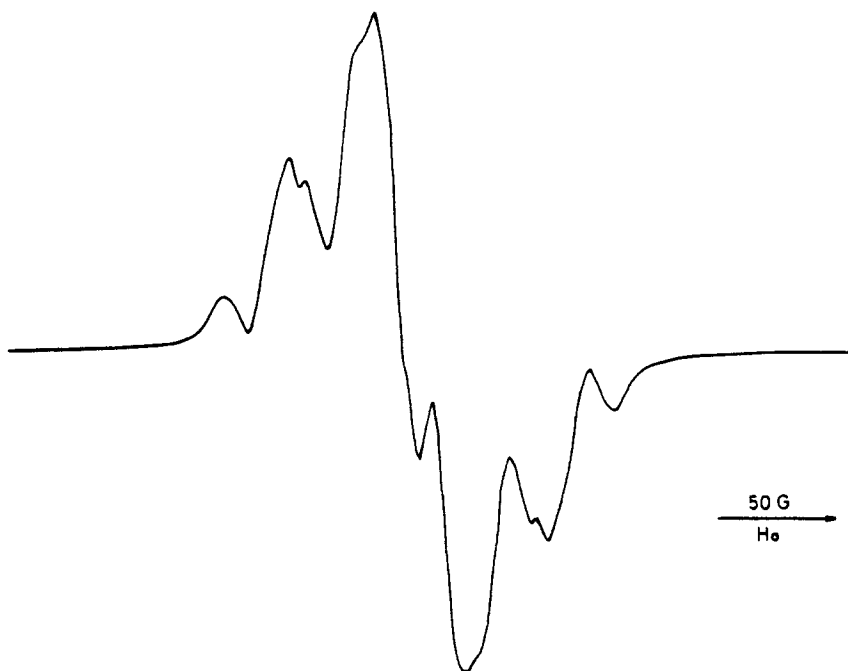The main difference in the decay curves in Figure 2 between the samples 1,

Fig. 1. ESR spectrum obtained with the sample treated as following. High-density polyethylene in the form of powder was first irradiated *in vacuo* at 298°K with a dose of 400 Mrad (sample 1). 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. ESR measurement was made at 77°K.

2, and 3 is above 270°K. In this temperature range, the decay curve is shifted to a higher temperature when the dose of first irradiation is increased. In order to clarify this difference, 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 4. This septet spectrum is attributed to allyl radicals. Figure 5 illustrates the conversion of alkyl radicals to allyl radicals[5] 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 240°K and increase in number to 300°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 6, the formation and decay of allyl radicals are compared for samples 1, 2, and 3. For the whole temperature range, the number of allyl radicals in sample 2 is the largest and that in sample 1 is the second largest. Obviously, the number of allyl radicals increases with increase of the first irradiation dosage.

Alkyl radicals abstract hydrogens next to the double bonds; allyl radicals newly produce and alkyl radicals disappear. When polyethylene is irradiated, double bonds are formed.[13,14] During the large first irradiation, many double bonds should be formed. The large number of double bonds react with alkyl radicals produced during the second irradiation to form many allyl radicals. These results show that, in the sample irradiated to a great extent, allyl radicals are much more important than in the sample not exposed to a large dose.
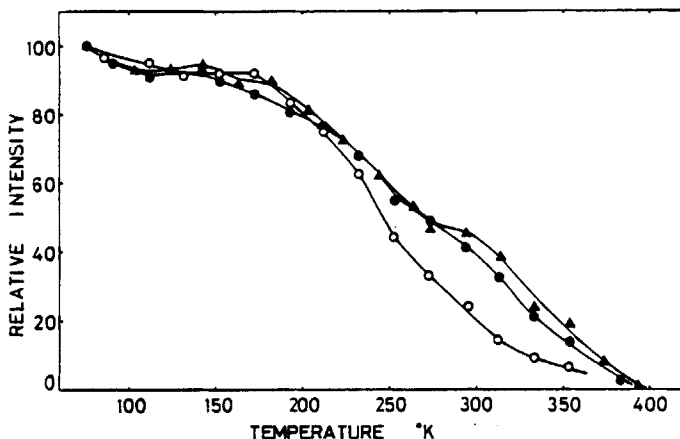
Fig. 2. Thermal decay curves of radicals produced by the second irradiation of 12.7 Mrad *in vacuo* at 77°K in following three samples: (●) high-density polyethylene in the form of powder was first irradiated with a dose of 400 Mrad (sample 1); (▲) same original sample irradiated with a dose of 638 Mrad (sample 2); (○) same original sample not exposed to a large dose (sample 3). After the first irradiations, radicals produced in samples 1 and 2 were destroyed. Samples 1 and 2 were evacuated again. These three samples were irradiated up to 12.7 Mrad *in vacuo* at 77°K. The samples irradiated at 77°K were heated to fixed temperatures for 5 min and cooled to 77°K for ESR measurements.

After the first irradiation, double bonds are densely distributed in the polymer matrix. The second irradiation at 77°K produce alkyl radicals. Two process can be considered for the decay reaction of these alkyl radicals produced by the second irradiation. One process is the reaction of alkyl radicals with double bonds. This process gives allyl radicals. The other process is the reaction of alkyl radicals without double bonds.

In the sample irradiated to a great extent, such as sample 1 or 2, many double bonds are stored in the polymer matrix. In these samples, the reaction of alkyl radicals with double bonds is a predominant process. Alkyl radicals are converted to allyl radicals effectively in this system. Allyl radicals are more stable
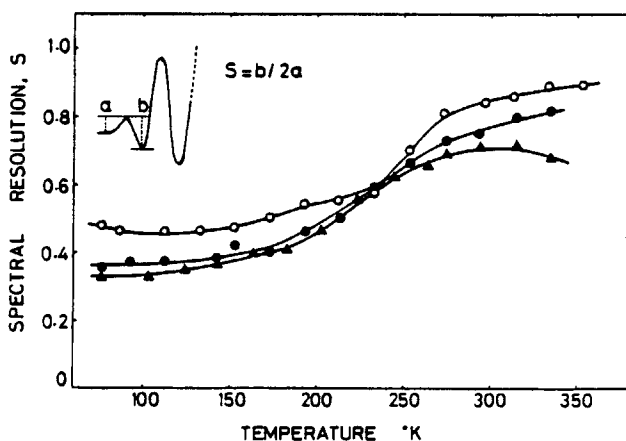

Fig. 3. The change in the degree of the spectral resolution denoted S in three samples (the same as those in Figure 2).
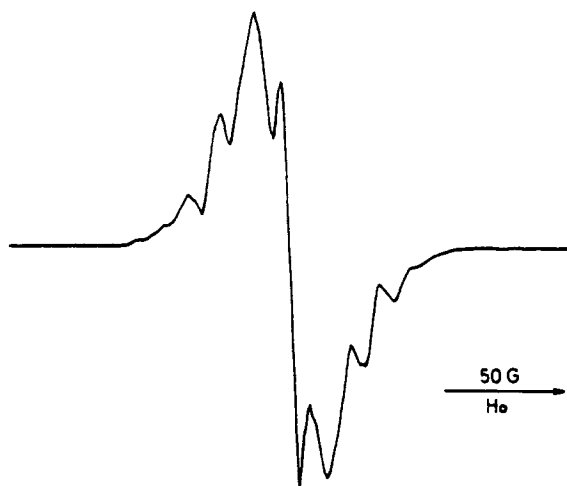
Fig. 4. "Sample 1" treated as the caption of Figure 1 was heated to 353°K for 5 min and cooled back to 77°K. ESR measurements were carried out at 77°K.

than alkyl radicals *in vacuo* at around 300°K. In this circumstance, accumulation of radicals easily occurs.

In the sample not exposed to a large dose, the conversion of alkyl radicals to allyl radicals is a less predominant process. In this sample, a predominant
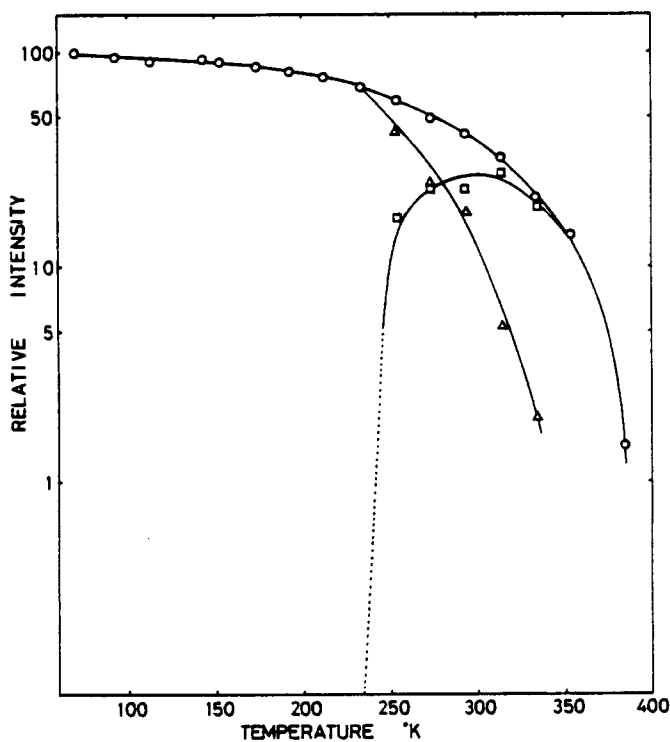

Fig. 5. Conversion of alkyl radicals to allyl radicals in the sample treated as the caption of Figure 2. The dosage of first irradiation was 400 Mrad. (sample 1): (O) total radical; (△) alkyl radical; (□) allyl radical.
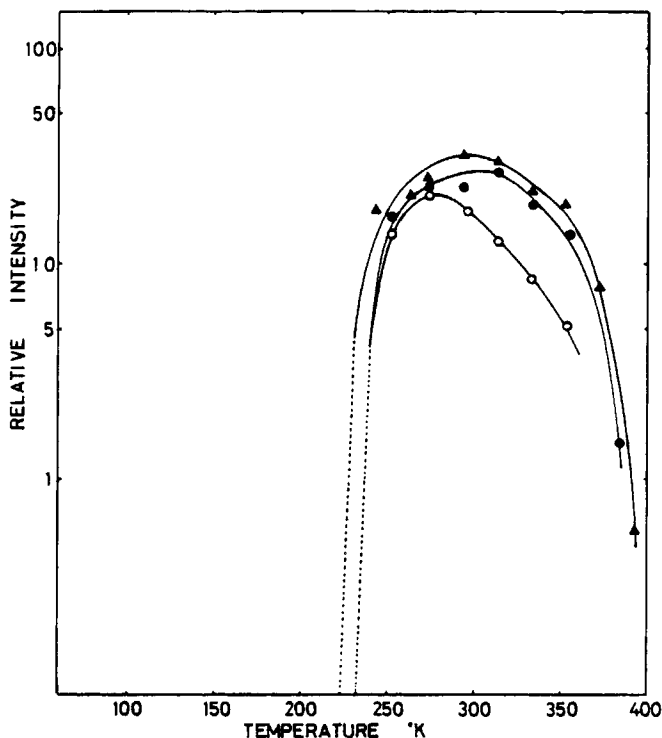
Fig. 6. The formation and decay of allyl radicals in the samples treated as the caption of Figure 2. First irradiation dosage: (●) 400 Mrad (sample 1); (▲) 638 Mrad (sample 2); (○) 0 Mrad (sample 3).

process is the decay of alkyl radicals by some types of reactions without formation of other radicals; for example, two alkyl radicals react together to form double bonds. In this system, it is hard for the accumulation of radicals to occur. The difference between the sample irradiated to a great extent and the sample not exposed to a large dose is the main cause of the difference of decay curves in Figure 2.

The method of double irradiation described above is not the actual case but is for the elucidation of the large-dosage irradiation effect. In the actual case, samples are irradiated at room temperature to a great extent during a long period. Note one point of time during the long period. Before this one point, samples have been exposed to a large dose. Many radicals have produced in the sample at room temperature and converted to stable products which contain double bonds. Many double bonds have already formed before this point. Alkyl radicals produced by the irradiation at this point react with the double bond already produced, and this reaction produce allyl radicals. The number of double bonds accumulated before this point increases as the dosage increases. The number of allyl radicals produced by unit irradiation dose at this point increases as the dosage before this point increases. This means that the accumulation rate of radicals increases with the increase of the dosage before this point.

This result, the increase of the rate of radical accumulation, is very important for the elucidation of large dosage irradiation because this result indicates accumulation of radicals could be accelerated. These radicals accumulated in a
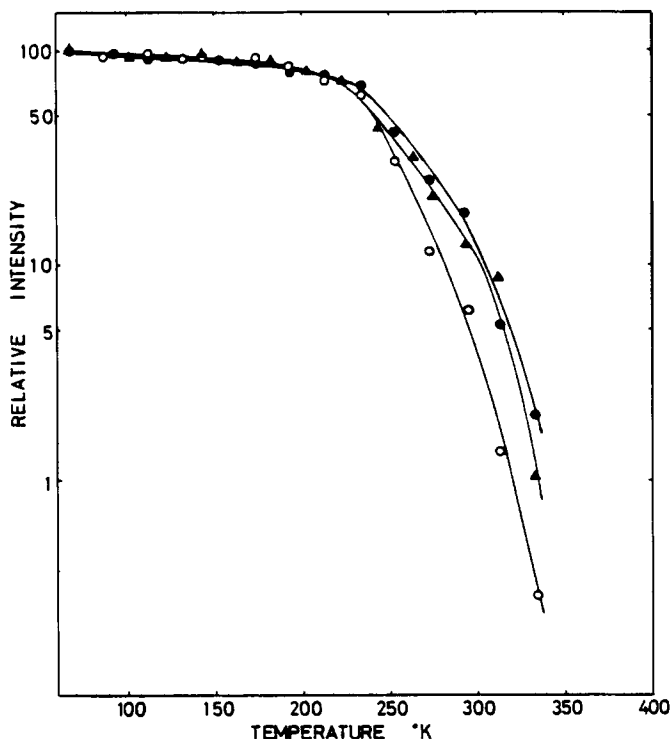
Fig. 7. Thermal decay curve of alkyl radicals in the samples treated as the caption of Figure 2. The dosage of first irradiation: (●) 400 Mrad (sample 1); (▲) 638 Mrad (sample 2); (○) 0 Mrad (sample 3).

large number affect the chemical and physical characteristics of the polymer exposed to a large dose. .

Figure 7 shows the decay curve of alkyl radicals after second irradiation. Above 250°K, the decay curve is the sample irradiated to a great extent shifted to a higher temperature. The amount of shift to a higher temperature increased as the dosage increased. This result can be explained as following. Irradiation produce crosslinks[15] in polyethylene. During the large first irradiation, many crosslinks are formed. These crosslinked networks make the polymer matrix more rigid before the second irradiation. In this sample, alkyl radicals produced by irradiation of a second time decay more slowly than those in the sample not exposed to a large dose. This rigidity in the polymer matrix also slows down the decay of allyl radicals. These slower decay rates of alkyl and allyl radicals also contribute to the acceleration in the accumulation rate of radicals in the sample irradiated to a great extent in the actual case.

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