

# Effect of an Additive on the Radiation Resistance of Polyethylene and Ethylene-Propylene Copolymer

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## Synopsis

In low-density polyethylene containing the additive propylfluorancene, radiation energy received by polyethylene is transferred to propylfluorancene, and the production of radicals at 77 K in polyethylene is suppressed. Propylfluorancene also increases the rate of the decay of radicals of polyethylene at room temperature. The depression of radical production and acceleration of radical decay at room temperature results in the depression of gas production and crosslinks at room temperature in low-density polyethylene containing propylfluorancene. Similar results were obtained in ethylene-propylene copolymer containing the same additive.

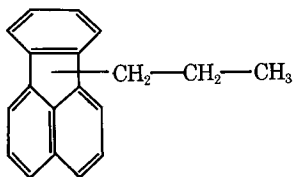
## INTRODUCTION

When polymers are irradiated with high-energy radiation, active species such as radicals, ions, and excited states were formed. These species react together and cause radiation effects<sup>1</sup> such as crosslinks, main-chain scission, and double bond formation which lead to degraded polymer. Some kinds of additives<sup>2,3</sup> have been added to polymers in order to prevent their deterioration.

The aim of the present work is to clarify the role of propylfluorancene on the radiation effect.<sup>4,5</sup> The results of our investigation identify the products after the radiation, gas evolution, crosslinks, and the behavior of radicals during the radiation chemical reaction.

## EXPERIMENTAL

**Materials.** The following samples were used: low-density polyethylene, Ube 520N (density 0.920; the methyl branch 1.7 per 100 carbon atoms); and ethylene-propylene copolymer. The additive propylfluorancene<sup>2</sup> was added to low-density polyethylene or ethylene-propylene copolymer by the mix-roll method. A sheet 0.5 mm thick was formed by hot-press molding.



Structure of propylfluorancene.

TABLE I  
Gas Evolution in Low-Density Polyethylene Irradiated up to 25 Mrad *in vacuo* at Room Temperature (*G*-Value)

Gas evolution	PE	PE + additive (7 parts)
Total gas	3.5	1.7
H <sub>2</sub>	3.4	1.7
C <sub>2</sub> H <sub>6</sub>	$3.5 \times 10^{-2}$	$6.2 \times 10^{-3}$
C <sub>4</sub> H <sub>10</sub>	$2.8 \times 10^{-2}$	$4.9 \times 10^{-3}$
C <sub>5</sub> H <sub>12</sub>	$8.0 \times 10^{-3}$	$1.6 \times 10^{-3}$
CH <sub>4</sub>	$6.8 \times 10^{-3}$	$2.6 \times 10^{-3}$
C <sub>2</sub> H <sub>4</sub>	$4.3 \times 10^{-3}$	$2.2 \times 10^{-3}$

**Electron spin resonance (ESR).** ESR measurements were carried out with a Varian V-4502 with field modulation of 100 kHz, and the input of microwave was between 0.15 and 0.13 mW. The measurement temperatures were 77 K or room temperature.

**Mass analysis.** Mass analysis was carried out with a Hitachi RMU-6 type mass spectrometer.

**High-resolution NMR.** NMR spectra were recorded by a JEOL PS-100 spectrometer operating at 100 MHz. Samples were resolved in tetrachloroethylene and measured at 373 K.

**Irradiation.** Samples used were evacuated up to  $10^{-6}$  torr and irradiated at room temperature or 77 K with  $\gamma$ -rays from a <sup>60</sup>Co source at a dose rate of 0.7–1 Mrad/h.

## RESULTS AND DISCUSSION

### Radiation Effects in Irradiated Low-Density Polyethylene and Ethylene-Propylene Copolymer

When the low-density polyethylene Ube 520N was irradiated *in vacuo* at room temperature with  $\gamma$ -rays from a <sup>60</sup>Co source up to 25 Mrad, gaseous products were evolved (Table I). Almost all of the gaseous products were hydrogen gas and a little amount of hydrocarbons. In the samples of polyethylene containing 7 parts propylfluorancene per 100 by weight, the amount of total gas and hydrogen is half that in the pure polyethylene. The amount of total gas evolved decreases as the amount of propylfluorancene in the polyethylene increases (Table II). Obviously, the evolution of hydrogen gas is suppressed by propylfluorancene.

TABLE II  
Relationship between *G*-Value of Total Gas Evolution and the Amount of Additive in Low-Density Polyethylene Irradiated *in vacuo* at Room Temperature

Amount of additive, parts	<i>G</i> -Value
0	3.5
1	2.2
3.5	1.7
7	1.7

High-resolution NMR spectra of the sample irradiated *in vacuo* at room temperature up to 100 Mrad are shown in Figure 1. The peak is due to the methylene unit  $-\text{CH}_2-$ . When the sample was not irradiated, the line width of the peak due to the methylene unit in the pure polyethylene was consistent with that in the polyethylene containing propylfluorancene. When the sample was irradiated, the line width of the peak due to the methylene unit in both systems, pure polyethylene and polyethylene containing propylfluorancene, was broader than that when the sample was not irradiated. In the irradiated system, the line width of the peak due to the methylene unit in the pure polyethylene was broader than that in the polyethylene containing propylfluorancene. The line width of the peak due to the methylene unit reflects the degree of the molecular motion of polyethylene. The broader the line width, the less mobile the polymer matrix. The lack of mobility in the pure polyethylene irradiated *in vacuo* indicates that pure polyethylene is highly crosslinked.<sup>6</sup> On the other hand, a narrower peak in the polyethylene containing propylfluorancene indicates that the crosslink reaction is depressed. In the case of the ethylene-propylene copolymer system, similar results were obtained (Fig. 2). Crosslinking is also depressed in the ethylene-propylene copolymer containing propylfluorancene.

### Radical Behavior at Low Temperatures

In order to clarify the mechanism for the depression of radiation effects in the irradiated polyethylene containing propylfluorancene, the following experiments with ESR were carried out. Figure 3 shows ESR spectra of low-density polyethylene irradiated *in vacuo* up to 15 Mrad at 77 K. Figure 3(a) is the spectrum of the pure polyethylene, and Figure 3(b) is the spectrum of the polyethylene containing 7 parts of propylfluorancene. In the case of Figure 3(b), the amount

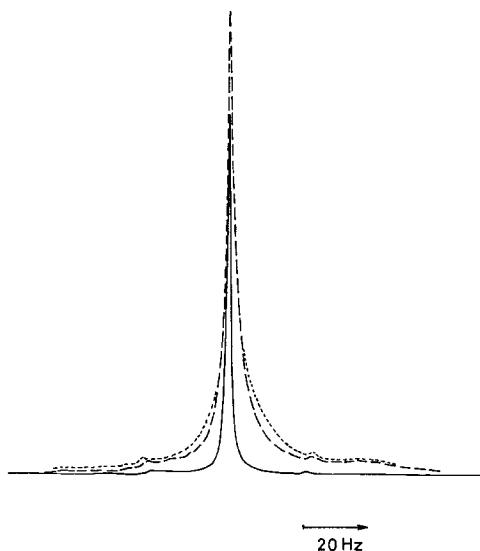


Fig. 1. High-resolution NMR spectra obtained with low-density polyethylene irradiated up to 100 Mrad *in vacuo* at room temperature: (—) unirradiated, both sample with propylfluorancene and without propylfluorancene; (.....) irradiated, without propylfluorancene; (---) irradiated, with 7 parts propylfluorancene.

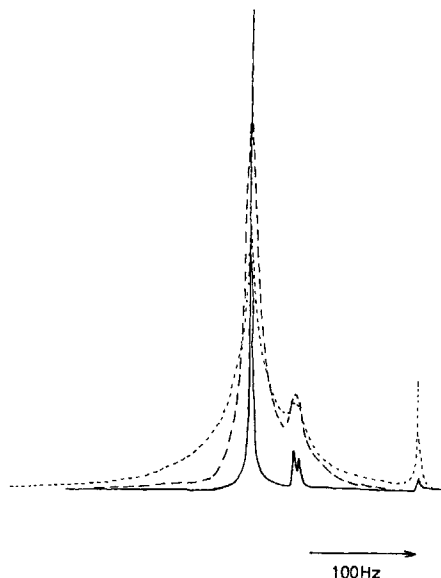


Fig. 2. High-resolution NMR spectra obtained with ethylene-propylene copolymer irradiated up to 200 Mrad in nitrogen atmosphere at room temperature: (—) unirradiated, both sample with propylfluorancene and without propylfluorancene; (.....) irradiated, without propylfluorancene; (- -) irradiated, with 5 parts propylfluorancene.

of sample was 1.2 times that of the sample in Figure 3(a). The concentration of radicals in the polyethylene containing propylfluorancene was to a large extent lower than that in the pure polyethylene. Consequently, the radical production was depressed in the polyethylene containing propylfluorancene. Both ESR spectra, Figures 3(a) and 3(b), are due to alkyl radicals produced in polyethylene. When the pure polyethylene and the polyethylene containing propylfluorancene were irradiated at 77 K up to 100 Mrad, the radicals accumulated, as shown in Figure 4. Up to 100 Mrad, the concentration of the radicals in the polyethylene containing propylfluorancene was lower than that in pure polyethylene, indicating that the propylfluorancene is effective up to a dosage of 100 Mrad.

The concentration of radicals produced in polyethylene irradiated in vacuo up to 15 Mrad at 77 K is shown in Table III. Evidently, there is a marked tendency for the yield of radicals to decrease as the amount of propylfluorancene increases. Furthermore, the concentration of radicals did not decrease when the samples were stored at 77 K overnight. In the case of the irradiated ethylene-propylene copolymer system, the amount of radicals also decreased when the amount of propylfluorancene increased (Table IV).

TABLE III  
Relationship between Radical Yield and the Amount of Additive in Low-Density Polyethylene Irradiated up to 15 Mrad *in vacuo* at 77 K

Amount of additive, parts	G-Value (radical)
0	3.0
1	2.4
3.5	2.3
7	2.3

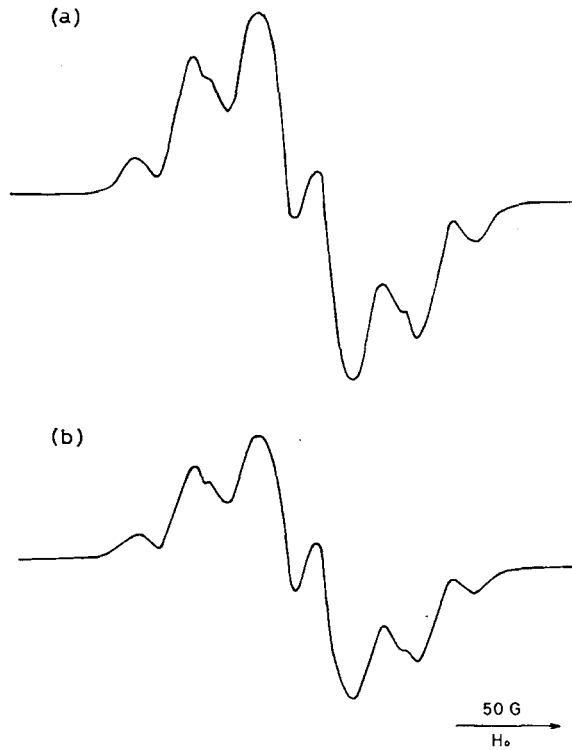


Fig. 3. ESR spectra obtained with low-density polyethylene irradiated up to 15 Mrad *in vacuo* at 77 K: (a) sample without propylfluorancene; (b) sample with 7 parts propylfluorancene. The amount of sample (b) is 1.2 times that in (a).

Part of the deposited radiation energy on polyethylene or ethylene-propylene copolymer, which is used to produce radicals of polyethylene or ethylene-propylene copolymer, is transferred<sup>7-10</sup> to propylfluorancene. This energy transfer

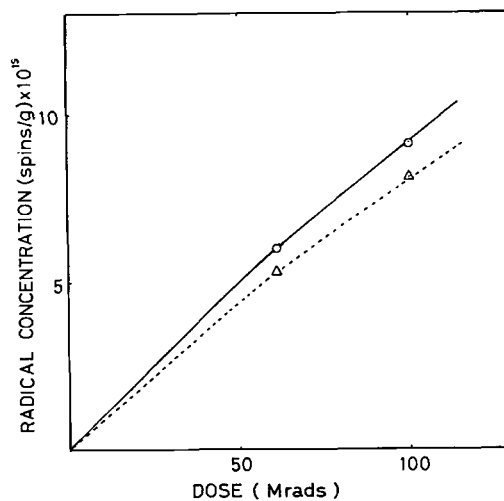


Fig. 4. Dose dependence of radical concentration in low-density polyethylene irradiated *in vacuo* at 77 K: (—) sample without propylfluorancene; (---) sample with 7 parts propylfluorancene.

TABLE IV  
Relationship between Radical Yield and Amount of Additive in Ethylene-Propylene Copolymer  
Irradiated up to 15 Mrad in Vacuo at 77 K

Amount of additive, parts	Relative radical yield, %
0	100
2	82
5	65

reduces the yield of radicals. The decrease in radical yield at 77 K results in the depression of gas production and crosslinks at room temperature. The energy absorbed by propylfluorancene is consumed as thermal vibrational energy in propylfluorancene.

When polyethylene irradiated at 77 K was heated and cooled back to 77 K for measuring, the spectrum varied both in shape and in intensity.<sup>11,12</sup> The variation in relative intensity with heating temperature is shown in Figure 5. In this figure, the radical yield at 77 K in the pure polyethylene was set at 100. The radical field at 77 K in the polyethylene containing propylfluorancene is about 70% of that in the pure polyethylene. The difference in radical amount between the two systems is large in the region of low temperature and small in the region of high temperature (Fig. 5).

Three decay regions of alkyl radicals have been reported in high-density polyethylene.<sup>11</sup> The first, second, and third decay regions have been connected with the decay of radical pairs, decay of radicals trapped in the surface of crystal or the defect of the crystal, and decay of radicals trapped in the crystalline region.<sup>11</sup> In the present experiment, the first decay region is around 100 K, the second around 130 K, and the third decay region above 190 K. The greatest difference in the decay curve between the pure polyethylene and the polyethylene containing propylfluorancene is observed in the second decay region. The alkyl radicals trapped in the surface of the crystal, the defect in the crystal, or the amorphous region of the pure low-density polyethylene are depressed most effectively. The radicals produced in the crystalline region connected with the

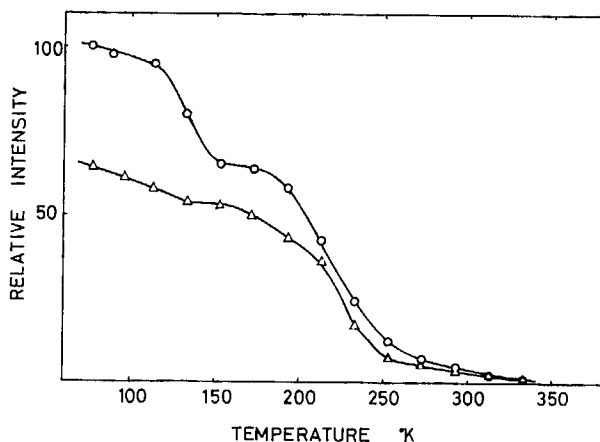


Fig. 5. Decay curves of radicals produced in low-density polyethylene irradiated at 77 K. Sample irradiated at 77 K was heated and cooled back to 77 K for ESR measurements: (—○—) sample without propylfluorancene; (—△—) sample with 7 parts propylfluorancene.

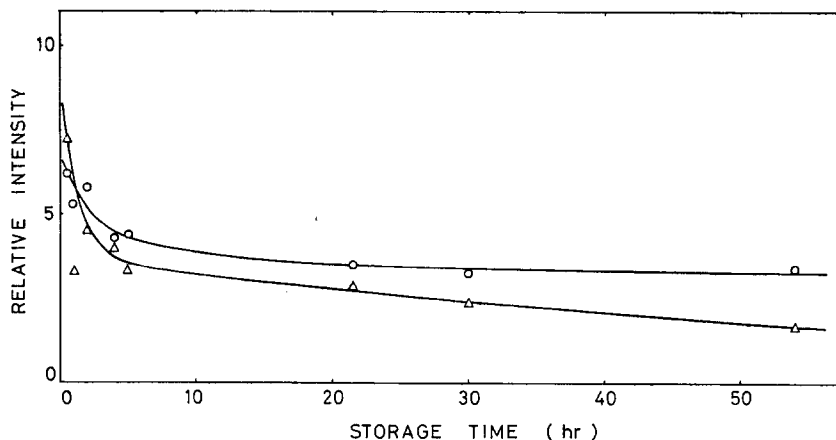


Fig. 6. Change of radical concentration in low-density polyethylene irradiated up to 15 Mrad *in vacuo* at 77 K and stored at room temperature: (—○—) sample without propylfluorancene; (—△—) sample with 7 parts propylfluorancene.

third decay region are slightly depressed. These facts are consistent with the assumption that propylfluorancene is added to the surface of the crystal, to the defect in the crystal, or to the amorphous region more effectively than to the crystalline region. The formation of radical pair,<sup>11</sup> connected with the first decay region is not depressed.

### Radical Behavior at Room Temperature

When the sample irradiated in *vacuo* at 77 K was stored *in vacuo* at room temperature for a long time, the alkyl radicals produced decay (Fig. 6). Some alkyl radicals are recombined to decay, and other alkyl radicals are converted to allyl radicals.<sup>12</sup> These allyl radicals also decay very slowly *in vacuo* at room temperature. After storing for a long time, the decay of allyl radicals was larger in the polyethylene containing propylfluorancene than in the pure polyethylene. Propylfluorancene, therefore, increases the rate of radical decay.

Radicals of propylfluorancene are combined with the radicals of the polyethylene. This suggestion is supported by the observation that the radicals of propylfluorancene decayed together with the radicals of polyethylene. Propylfluorancene reduces radical formation at 77 K, as shown in the previous section. However, propylfluorancene could not eliminate all radical formation at 77 K. It is also important for radiation resistance that the additive increases the decay of radicals more quickly at room temperature.

The present work indicates that propylfluorancene depresses the formation of radicals from polyethylene and increases the rate of decay of these radicals.

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