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The Radical Formation of Polyethylene by Tesla Discharge

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Synopsis. The ESR spectra of polyethylene discharged by a Tesla coil in an atmosphere of various gases were observed. An alkyl radical showing a six-line spectrum was formed in the Tesla discharge at 77 K, whereas a polyenyl radical was mainly produced by the discharge with an increase in the duration time; these facts showed that the effects of the Tesla discharge were similar to the γ-irradiation up to a high dose.

Many studies of the radical formation of polyethylene by γ-irradiation have been done.[1-6] The results of these works have revealed that at least three kinds of radicals are produced in polyethylene irradiated at room temperature. A radical with a short life-time gives a sextet spectrum and is identified with the alkyl radical, $-CH_2-\dot{C}H-CH_2$. A radical with a longer life-time shows a septet spectrum and is assigned to the allyl radical, $-CH_2-\dot{C}H-CH=CH-CH_2-$. The third radical has a very long life-time and gives a singlet spectrum, identified with the polyenyl radical, $-CH_2-\dot{C}H(-CH=CH)_n-CH_2-$. The alkyl and allyl radicals are the main products in γ-ray irradiation, whereas in the case of a high-dose irradiation the polyenyl radical is mainly formed.

On the contrary, the mechanism of the radical formation of polyethylene in a discharge has not been revealed. Our purpose in this work is to confirm that it is reasonable to interpret discharge chemistry from the standpoint of radiation chemistry.

H_2, N_2, and Ar gases with a high purity were used without further purification. The He gas was purified according to Polley's cold-charcoal-trap method.[7] The polyethylene used in these experiments was HZ 5000p, supplied by the Mitsui Petroleum Chemical Co. as powder. This powder sample was evacuated for 50 hr *in vacuo*. After the introduction of each gas (0.3 Torr), the sample tube was cut off. γ-Irradiation at a dose rate of 3×10^3 r/hr and a discharge by using a Tesla coil were carried out in the Pyrex-glass part of the sample tube at 77 K, while the ESR spectra were measured in the quartz-glass part at the same temperature. The ESR spectra were observed by using a Japan Electron Optics Laboratory JES-3BS-X-type spectrometer at a microwave frequency of 9400 MHz, with a 100 kHz field modulation. The gas products from irradiated and discharged polyethylene were measured by using a Hitachi-RMU-6D mass spectrometer.

It is well known that the alkyl radical formed by the γ-irradiation of unstretched polyethylene shows a six-line spectrum. It is interpreted as resulting from the abstraction of a hydrogen atom from the middle of a linear polyethylene[8] and from the apparent equal coupling of the unpaired electron to α-and β-hydrogen.[9,10]

Figure 1 shows the first derivative curve and the integrated curve of the ESR spectrum of the radical pro-

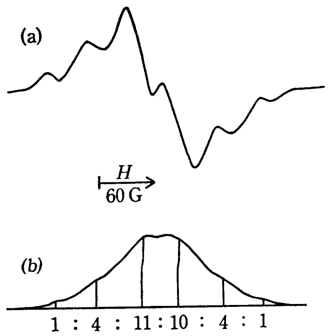

Fig. 1. ESR spectrum of radical produced by Tesla discharge at 77 K.
(a): First derivative curve, (b): Integrated curve.

duced by Tesla discharge in an atmosphere of H_2 gas (0.3 Torr). The ESR spectrum with a hyperfine coupling constant of 30 gauss is similar to that of γ-irradiated polyethylene.[11] Furthermore, the absorption-peak intensity ratio of the sextet in the integrated curve was 1:4:11:10:4:1. This ratio is in good agreement with the theoretical ratio for the alkyl radical, 1:5:10:10:5:1. Thus, it can be concluded that, in the Tesla discharge, the alkyl radicals are mainly formed, as in radiolysis. In an atmosphere of N_2, He, and Ar gasses, the same spectra were observed, although the peaks differed in sharpness.

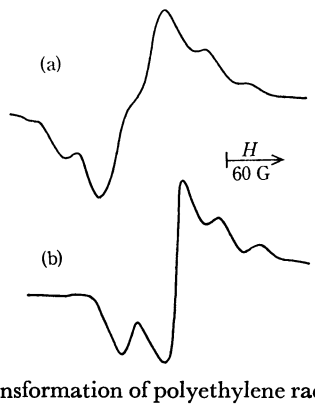

Fig. 2. Transformation of polyethylene radical generated by the dischage to peroxy radical.
(a): After the immersion into a dry-ice bath for 60 s.
(b): After exposure to air for 60 s in a dry-ice bath.

When polyethylene discharged at 77 K was exposed to air at its temperature, the ESR spectrum was almost the same as the original. Figure 2(a) shows the ESR spectrum of the discharged polyethylene after immersion into a dry-ice bath for 60 s. Although there was an appreciable loss in signal, there was little or no change in line shape. The spectrum in Fig. 2(b) represents the behavior of the alkyl radical when exposed to air for 60

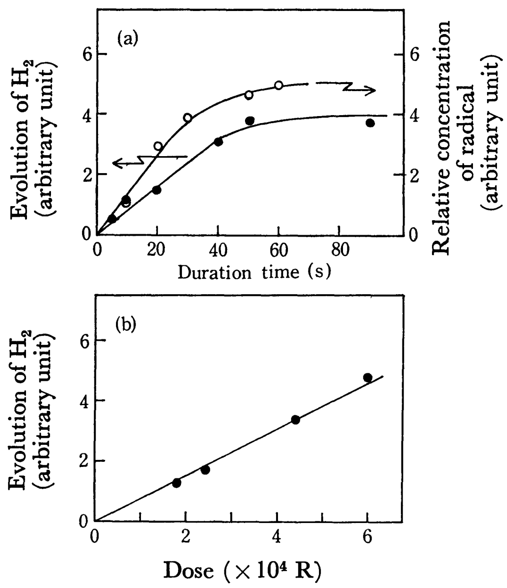

Fig. 3. Evolution of H_2 gas *vs.* duration time and dose. (a): Discharge, (b): γ-Irradiation.

s under the same conditions. It has been found that many of the polymer radicals react with oxygen to form peroxy radical.[11] Thus, the singlet line in the central part of the spectrum, which is superimposed on the spectrum attributable to the alkyl radical, represents the peroxy radical.

A relatively major quantity of H_2 gas and a trace amount of CH_4 gas were detected from the discharged polyethylene, whereas only the H_2 gas was observed from the γ-irradiated polyethylene. Lawton *et al.* have revealed the mechanism of H_2-gas evolution in γ-irradiated polyethylene.[12] Figure 3 shows the amount of H_2 gas evolved against the duration time and the irradiation dose. In the case of discharge, the amounts remained constant 50 s. The relative concentration of the alkyl radical also similarly became constant. On the contrary, in the case of γ-irradiation the amount of H_2 gas increased linearly with an increase in the irradiation dose. Figure 4 shows the ESR spectra of polyethylene with an increase in the duration time of discharge and in the irradiation dose of the γ-rays. The ESR spectrum of polyethylene discharged for 120 s ill-resolved, and the overall line-width of the spectrum of polyethylene discharged for 300 s is smaller than that in Fig. 4(b), suggesting that the alkyl radical is transformed with the dose to another radical, probably one with a singlet absorption. In the polyethylene irradiated with high dose γ-rays, the spectrum containing a six-line (4(d)) is transformed to a singlet with a smaller overall line width (4(e)). The latter spectrum is assigned to the polyenyl radical.[13] Thus, the ESR spectrum of polyethylene discharged for a long duration time is presumed to be attributable to the polyenyl radical, as in radiolysis. Although we could not find any precise correspondence between the Tesla discharge and the γ-irradiation, from these results it was semiquantitatively ascertained that their effects were similar to each other up to a high dose.

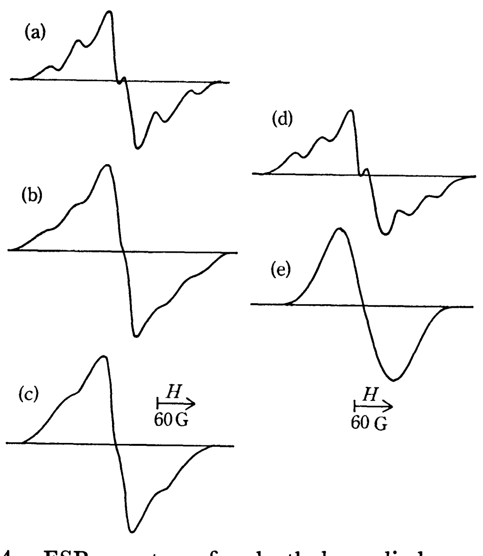

Fig. 4. ESR spectra of polyethylene discharged and irradiated with an increasing duration time and dose. (a): Discharge for 10 s, (b): 120 s, (c): 300 s, (d): γ-Irradiation with 8 MR, (e): 1000 MR.

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