

SHORT COMMUNICATION

Pressure Dependence of Methyl Radical Observation in Polypropylene Irradiated by Ultraviolet Light

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In a previous paper¹ we reported the pressure dependence of radical formation in polyethylene irradiated by ultraviolet light. The apparent singlet spectrum was observed from the sample evacuated to 10^{-6} mmHg after ultraviolet irradiation at -196°C , while the six-line spectrum was mainly observed from the poorly evacuated samples. This difference was tentatively attributed to change in the energy transfer mechanism.

It is reported^{2,3} that ESR spectrum due to methyl radicals was observed after ultraviolet irradiation of polypropylene at -196°C . In this communication we want to report that methyl radical observation in polypropylene depends upon the pressure in the sample tube.

Polypropylene (Sumitomo Chemical Co., Ltd. FS-100) was purified by dissolving it in boiling toluene, precipitated by cooling and washing with methanol and *n*-hexane. These procedures were repeated twice. Rod-shaped specimens of 2 mm square were obtained by pressing the purified sample of polypropylene at 180°C between stainless-steel frames. These specimens were immersed in *n*-hexane for over two days. The sample was evacuated to 10^{-6} mmHg in the sample tube at about 90°C , and subsequently nitrogen gas was introduced at various pressures. Ultraviolet irradiations were carried out at -196°C by using a Xenon short arc lamp (Ushio Electric Inc. UXL-500D) in a lamp house (UI-501), which was apart about 60 cm from the sample. ESR spectra were recorded at -196°C by an X-band spectrometer with 100 kc field modulation (Japan Electron Optics Lab. Co., model JES, 3BS-X).

The sample evacuated to 10^{-5} mmHg was

irradiated at -196°C for about half an hour. A spectrum shown in Figure 1(a) was observed during irradiation, and this spectrum seems to be

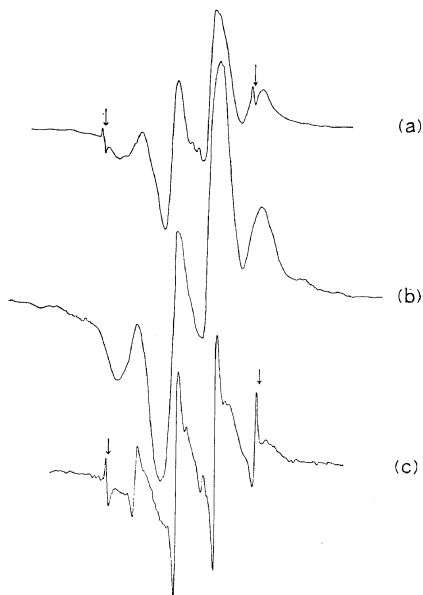


Figure 1. ESR spectra of polypropylene irradiated by ultraviolet light at -196°C .

- (a): Pressure in the sample tube. 10^{-5} mmHg, $G = 250$
- (b): After keeping the sample (a) at -196°C for 10 days, $G = 500$
- (c): Pressure in the sample tube: 10^{-1} mmHg, $G = 250$

G represents an amplifier gain setting.

The spectra (a) and (c) were recorded during irradiation. Arrow marks indicate the absorption peaks due to Mn^{++} , whose separation is 86.7 gauss.

predominantly a four line spectrum with a coupling constant of about 25 gauss. A small amount of a six line spectrum, however, may superpose.

The four line spectrum can reasonably be

attributed mainly to free radicals $-\text{CH}_2-\overset{\cdot}{\text{C}}\text{H}-\text{CH}_2-$ (I)⁴, although there may be some other possible free radicals to give the four line spectrum.^{2,3} The six-line spectrum can be attributed to free radicals $-\text{CH}_2-\overset{\cdot}{\text{C}}\text{H}-\text{CH}_2-$ (II).³

After the sample was kept for 10 days at -196°C , the spectrum shown in Figure 1(a) changed into an eight line spectrum with a coupling constant of about 27 gauss as shown in Figure 1(b). This can be attributed mainly to free radicals $-\text{CH}_2-\overset{\cdot}{\text{C}}(\text{CH}_3)-\text{CH}_2-$ (III). This change is caused by a radical conversion⁴ and it will be discussed in a later paper.

On the other hand, under the same experimental conditions, the sample with nitrogen gas pressure of 10^{-1} mmHg gave a spectrum shown in Figure 1(c) in which the four-line spectrum due to methyl radicals can easily be distinguished besides the broad component of the spectrum. The four-line spectrum due to methyl radicals decayed out after the sample was kept at -196°C for a few days, and there remained a spectrum similar to that shown in Figure 1(a).

It was found that methyl radicals were observed from all the samples of vacuum lower than 10^{-2} mmHg.

The sample evacuated to 10^{-6} mmHg did not give methyl radicals even after a relatively longer time of irradiation. However once the irradiated sample was warmed up to room temperature, at which temperature most of the free radicals disappeared, and was recooled to -196°C , methyl radicals were observed after the subsequent irradiation. The pressure in the sample tube was found to increase over 10^{-2} mmHg when the sample was warmed to room temperature. Therefore the fact that methyl radicals were observed upon further irradiation can also be explained by change of the pressure in the sample tube.

There are two possible mechanisms to explain the pressure dependence of methyl radical observation. The first one is to assume that no

methyl radicals were produced in the highly evacuated samples probably because of the different energy transfer mechanisms from that in the poorly evacuated samples. The second one is to consider that methyl radicals vanished in the highly evacuated samples by a mechanism not immediately apparent even if they were produced once by ultraviolet irradiation.

Different energy transfer mechanisms have been proposed¹¹ between in the highly- and poorly-evacuated samples of polyethylene in order to explain an observation of different ESR spectra in each case. In the present case, however, the broad component (Figure 1(a)) was observed from both high- and low-vacuum samples. Therefore the same mechanism as proposed for polyethylene can not be applicable to polypropylene, and an exact mechanism along this line is not settled. In order to examine the second possibility, the following experiments were carried out: The sample which showed the ESR spectrum of methyl radicals was evacuated at -196°C to 10^{-5} mmHg for about half an hour. Only a small amount of methyl radicals decayed out during this procedure. It was found, however, that the ESR spectrum due to methyl radicals disappeared quickly by further ultraviolet irradiation. Therefore it is evidenced that methyl radicals disappear in a highly evacuated sample by ultraviolet irradiation even if they are produced as a primary event. This may be caused by excitation of methyl radicals by ultraviolet light. Methyl radicals are relatively small and they will be able to escape from their trapping sites by excitation and to move more readily in higher vacuum,⁵ resulting in recombination. This mechanism is consistent with the fact that the broad component due to the free radicals (I) and (II), which cannot diffuse so easily, was not much influenced by the change in the pressure. It is also known that methyl radicals were not observed after irradiation of polypropylene by high energy radiation, and this was attributed similarly to the fact that ionizing radiation imparts excessive energy to the methyl radicals.²

Therefore the pressure dependence of methyl radical observation in polypropylene can be explained by the fact that methyl radicals decay out quickly by ultraviolet irradiation in high vacuum

but not in low vacuum, and this mechanism seems to be prevailing, although the possible change in the energy transfer mechanism cannot be excluded.

Further description of this study will be published elsewhere.

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