Study on the Reaction Between Polymer Radical and 1, 1-Diphenyl-2-Picryl Hydrazyl

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1, 1-Diphenyl-2-picryl hydrazyl (DPPH) has been used as a radical scavenger for various reactions both in solution and in solid. In the present study, reactions between DPPH dispersed in polymethylmethacrylate film and radicals produced by irradiation of DPPH-polymer system, and the effect of oxygen on the reactions are investigated using the electron spin resonance spectroscopy.

The results are as follows: the rate of decomposition of DPPH by irradiation is the same both *in vacuo* and in the presence of air at a higher initial concentration of DPPH. At a lower initial concentration of DPPH, on the other hand, the decomposition is accelerated in the presence of air. This is due to the fact that the rate constant of the reaction of peroxy radical ($PO_2 \cdot$) with DPPH is larger than that of the initial polymer radical ($P \cdot$).

INTRODUCTION

1, 1-Diphenyl-2-picryl hydrazyl (DPPH) is a stable free radical which reacts with many other free radicals. It is assumed, and in certain cases has been shown, that one molecule of DPPH reacts with one radical. For this reason it has been frequently used as a radical scavenger for various reactions and its reactions in solutions have been studied by many workers such as Bawn[1], Uno[2], Hammond[3], Chapiro[4~6], Henglein[7~9] and Dainton[10].

In solid polymer, however, a radical scavenging reaction by oxygen may be assumed to be more efficient than that by DPPH since oxygen is more reactive than DPPH. Consequently the effect of air may be very important. Manabe and one of the present authors showed that the radical scavenging efficiency of DPPH in solid was smaller than that in solutions in the presence of air[11].

In the present study, reactions between DPPH dispersed in polymethylmethacrylate (PMMA) film and radicals produced by irradiation of DPPH-polymer system, and the effect of oxygen on the reactions are investigated using the electron spin resonance spectroscopy (ESR).

EXPERIMENTAL

Raw polymethylmethacrylate is precipitated twice from benzene with methanol and dried *in vacuo* for two weeks at room temperature.

1 : 1 DPPH-benzene molecular complex[11] is used after crushing in a morter.

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Polymer film containing DPPH is prepared as follows; PMMA is dissolved in a certain amount of benzene solution of DPPH and the solution is diluted with benzene to give a 2~3 wt.% solution. Then the solution is poured onto a glass plate and is left standing for about five hours to evaporate excess benzene.

The polymer film thus obtained is cut into pieces, put in a sample tube of a diameter of approximately 4 mmϕ, dried *in vacuo* (pressure less than 10^{-4} mm Hg) at room temperature and then sealed.

Two samples are duplicated to compare the radical concentration of the irradiated sample with the unirradiated one and to calculate the change of the radical concentration of the sample.

Gamma-ray irradiation is carried out at room temperature by 2000 Curie Co-60 gamma-ray irradiation facility of the Institute for Chemical Research and the dose-rate is 1.5×10^5 r/hr.

One end of the irradiated sample tube is heated before ESR measurement to avoid the effect of the radicals produced in a glass tube during the irradiation.

ESR measurements are carried out with a reflection type spectrometer with a H_{012} type sample cavity operating at 9400 Mc/sec. Microwave power less than 1 mW is used to avoid the saturation phenomena.

RESULTS

ESR pattern

Radicals are produced in PMMA by irradiation *in vacuo* at room temperature and show ESR patterns which are complicated line shapes with over-all line width of about 80 gauss.

The radicals decay gradually after the irradiation. Fig. 1 shows the decay of radicals produced by the irradiation *in vacuo* at a total dose of 1.85×10^7r.
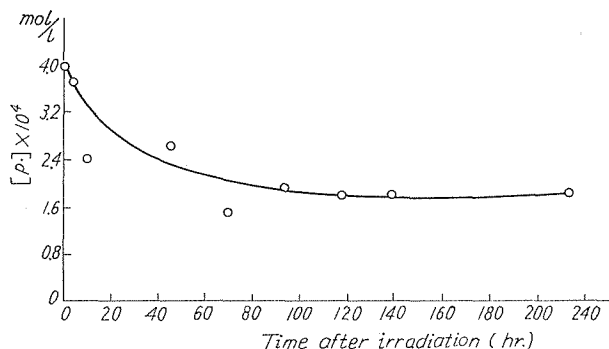

Fig. 1. Decay of PMMA radicals produced by irradiation *in vacuo* at room temperature at a total dose of 1.85×10^7r.

Radicals are detected in the case of irradiation *in vacuo* by ESR spectroscopy, but in the presence of air no trapped radicals are observed at the same total dose. In this case, the radicals produced by irradiation in the presence of air may react immediately with oxygen in the polymer and therefore are not detected.
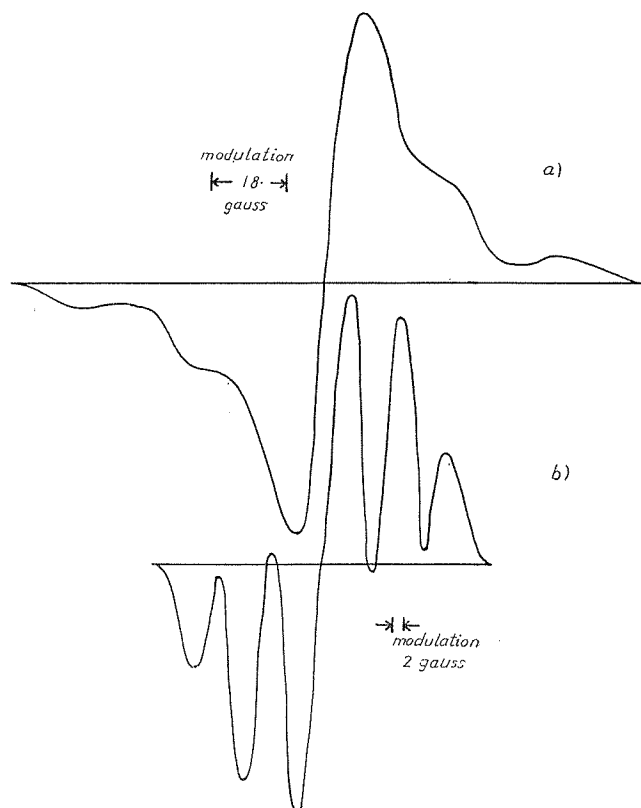
Fig. 2. ESR pattern of DPPH.
a) in polymer film $(0.7 \times 10^{-2}\,\text{mol}/1)$ line width 120 gauss.
b) in benzene solution $(0.5 \times 10^{-2}\,\text{mol}/1)$ line width 60 gauss.

ESR pattern of DPPH in the benzene solution is quintet with over-all line width of approximately 60 gauss, on the other hand, the pattern in polymer film is poor-resolved quintet with the width of approximately 120 gauss as shown in Fig. 2. This broadening is caused by the anisotropic hyperfine structure (hfs) in addition to the isotropic hfs because of rigidity of the polymer film.

Change of radical concentration by irradiation *in vacuo*

When the polymer containing DPPH is irradiated, purple color of DPPH becomes reddish brown as the color of products.

Fig. 3 shows the relationship between the irradiation time and radical concentration of DPPH-polymer system irradiated *in vacuo*. When the initial concentration of DPPH is very small, the total radical concentration of DPPH-polymer system decreases at first, and then increses gradually with the irradiation time. This radical concentration is a little larger than that of pure polymer system after 200 hours irradiation. It seems that the polymer radicals produced by irradiation can not completely be scavenged by DPPH. When the initial concentration of DPPH is large, a linear relation is observed between the irradiation time and total radical concentration.

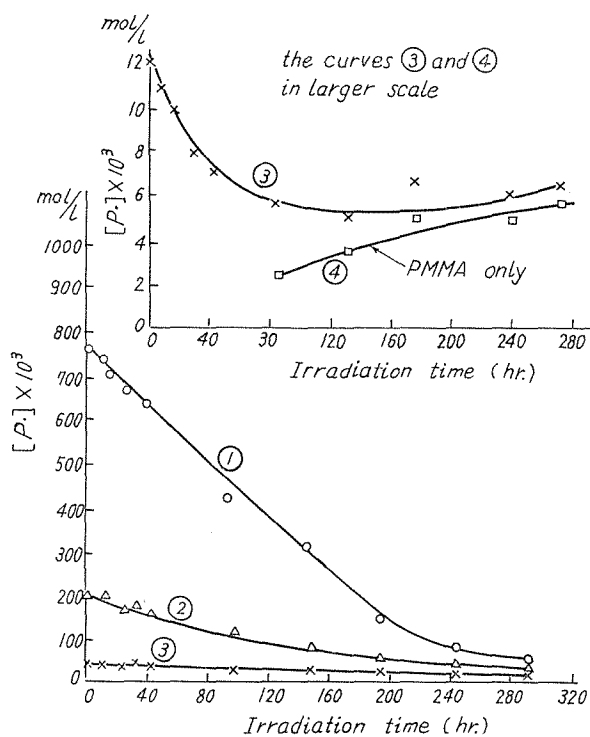Fig. 4 shows the relationship between the logarithm of total radical con-
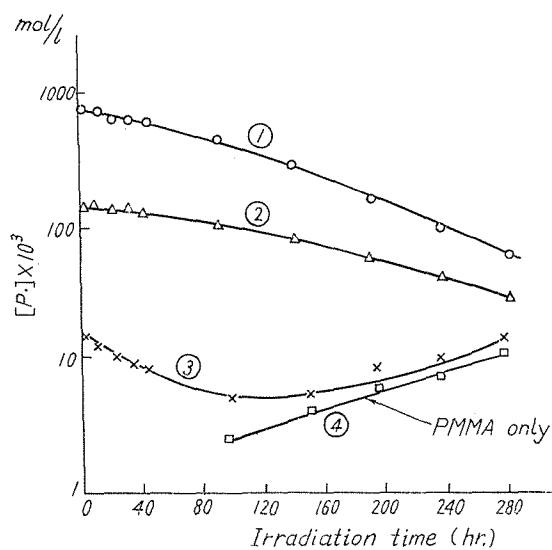
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Fig. 3. Change of radical concentration by irradiation *in vacuo.*

Fig. 4. Change of radical concentration by irradiation *in vacuo.*

centration and irradiation time. For the lowest initial concentration of DPPH, the linear decay at the initial step of irradiation is observed, and the radical concentration increases with the irradiation time at the later period. The phenomena are seemingly due to an offset of decrease in DPPH concentration by the increase in polymer radical concentration. The radical concentration will reach a certain stationary concentration eventually.
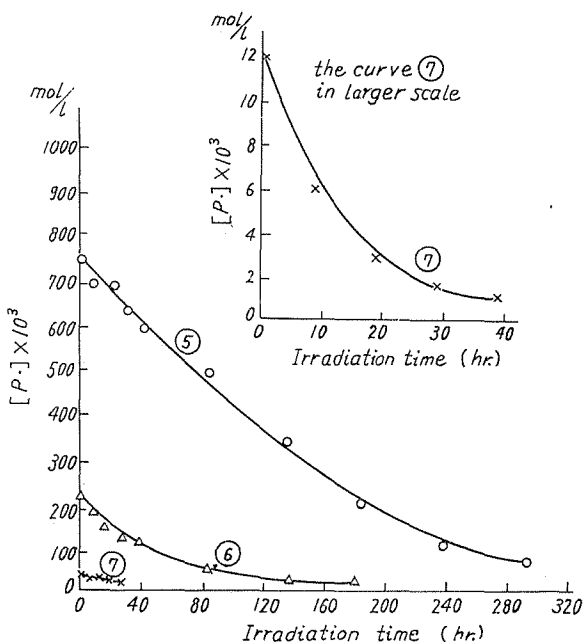

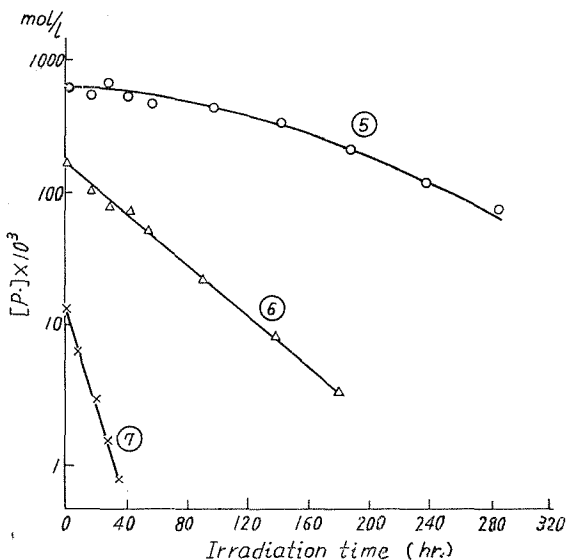Fig. 5. Change of radical concentration by irradiation in the presence of air.

Fig. 6. Change of radical concentration by irradiation in the presence of air.

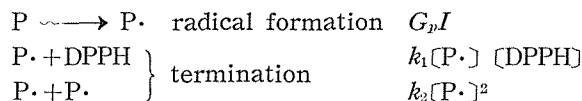**Change of radical concentration by irradiation in the presence of air**

Fig. 5 shows the relationship between the irradiation time and radical concentration in DPPH-polymer system irradiated in the presence of air. When the initial concentration of DPPH is high, a linear relation is observed between the radical concentration and irradiation time, and the slope is the same as that obtained *in vacuo*.

Fig. 6 shows the relationship between the logarithm of radical concentration and irradiation time. When the initial concentration of DPPH is very small, there is a linear relation as observed *in vacuo* but with a larger slope in absolute value. It seems that oxygen assists the decrease in DPPH concentration by a certain mechanism.

DISCUSSION

Kinetics of reactions *in vacuo*

In the case of irradiation *in vacuo*, a linear relation is observed at a higher initial concentration of DPPH between the radical concentration and irradiation time; and at a lower initial concentration of DPPH, between the logarithm of radical concentration and irradiation time. These results are explained by following kinetics with the assumption that the radical concentration observed are the same as that of DPPH.

When DPPH-polymer system is irradiated *in vacuo*, the following elementary reactions are assumed.

$$
\begin{aligned}
&\text{P} \rightsquigarrow \text{P}\cdot \quad \text{radical formation} \quad G_pI \\
&\left.\begin{array}{l}\text{P}\cdot + \text{DPPH} \\ \text{P}\cdot + \text{P}\cdot\end{array}\right\} \text{termination} \quad \begin{array}{l}k_1[\text{P}\cdot]\,[\text{DPPH}] \\ k_2[\text{P}\cdot]^2\end{array}
\end{aligned}
$$

where G_p is G value for the radical formation and I is the dose-rate. In the kinetics mentioned above, the direct effect of ionizing radiation on decomposition of DPPH is neglected because of the small fraction of DPPH in the system.

Assuming the stationary concentration of [P·], equation (1) is obtained.

$$G_pI = k_1[\text{P}\cdot]\,[\text{DPPH}] + k_2[\text{P}\cdot]^2 \tag{1}$$

At a higher DPPH concentration, the second term of eq. (1) is neglected with the assumption that most of the radicals produced by irradiation may be scavenged by DPPH.
Equations (2) and (3) are obtained.

$$G_pI = k_1[\text{P}\cdot]\,[\text{DPPH}] \tag{2}$$

$$[\text{P}\cdot] = G_pI/k_1\,[\text{DPPH}] \tag{3}$$

The rate of decrease in DPPH concentration is defined as

$$-d[\text{DPPH}]/dt = k_1[\text{P}\cdot]\,[\text{DPPH}] \tag{4}$$

Eq. (5) is obtained from eqs. (3) and (4).

$$-d[\text{DPPH}]/dt = G_pI \tag{5}$$

Consequently
$$[\text{DPPH}] = -G_pIt + [\text{DPPH}]_i \tag{6}$$

where $[DPPH]_0$ is the initial concentration of DPPH.

On the other hand, at a lower DPPH concentration, the first term of right-hand side of eq. (1) is neglected with the assumption that most of the radicals produced by irradiation may recombine each other. Eqs. (7) and (8) are obtained.

$$G_pI = k_2[P\cdot]^2 \tag{7}$$

$$[P\cdot] = (G_pI/k_2)^{1/2} \tag{8}$$

From eqs. (4) and (8), the rate of decrease in DPPH concentration is as follows;

$$-d[DPPH]/dt = k_1(G_pI)^{1/2}[DPPH]/k_2^{1/2} \tag{9}$$

Consequently $\quad \ln[DPPH] = -k_1(G_pI)^{1/2}t/k_2^{1/2} + \ln[DPPH]_0 \tag{10}$
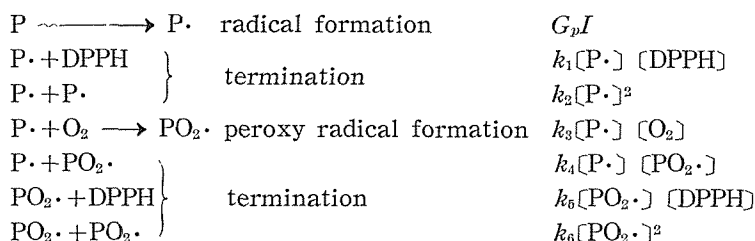
Thus it can be explained that the linear relation exists between the radical concentration and irradiation time at a higher DPPH concentration, and between the logarithm of radical concentration and irradiation time at a lower DPPH concentration. The slopes correspond to the values of $-G_pI$ and $-k_1(G_pI)^{1/2}/k_2^{1/2}$, respectively.

Kinetics of the reaction in the presence of air

In the case of irradiation in the presence of air, a linear relation is observed, at a higher initial concentration of DPPH, between the radical concentration and irradiation time with the slope nearly equal to that *in vacuo*: and at a lower initial concentration of DPPH, between the logarithm of radical concentration and irradiation time with a larger slope in absolute value than that *in vacuo*. These results are explained by following kinetics.

Any ESR signal is not observed in the case of irradiation of polymer in the presence of air. ESR signal of polymer irradiated *in vacuo* decays rapidly after introduction of air. From these facts, it is assumed that oxygen and polymer radicals react to give peroxy radicals[12,13] and that peroxy radicals react each other immediately after their formation.

The following elementary reactions are assumed.

$$\begin{array}{lll}
P \rightsquigarrow\!\!\longrightarrow P\cdot & \text{radical formation} & G_pI \\
\left.\begin{array}{l} P\cdot + DPPH \\ P\cdot + P\cdot \end{array}\right\} & \text{termination} & \begin{array}{l} k_1[P\cdot]\,[DPPH] \\ k_2[P\cdot]^2 \end{array} \\
P\cdot + O_2 \longrightarrow PO_2\cdot & \text{peroxy radical formation} & k_3[P\cdot]\,[O_2] \\
\left.\begin{array}{l} P\cdot + PO_2\cdot \\ PO_2\cdot + DPPH \\ PO_2\cdot + PO_2\cdot \end{array}\right\} & \text{termination} & \begin{array}{l} k_4[P\cdot]\,[PO_2\cdot] \\ k_5[PO_2\cdot]\,[DPPH] \\ k_6[PO_2\cdot]^2 \end{array}
\end{array}$$

Assuming the stationary concentration of $[P\cdot]$, eq. (11) is obtained.

$$G_pI = k_1[P\cdot]\,[DPPH] + k_2[P\cdot]^2 + k_3[P\cdot]\,[O_2] + k_4[P\cdot]\,[PO_2\cdot] \tag{11}$$

and also assuming the stationary concentration of $[PO_2\cdot]$, eq. (12) is obtained.

$$k_3[P\cdot]\,[O_2] = k_4[P\cdot]\,[PO_2\cdot] + k_5[PO_2\cdot]\,[DPPH] + k_6[PO_2\cdot]^2 \tag{12}$$

Eq. (13) is obtained from eqs. (11) and (12).

$$G_pI = k_1[P\cdot]\,[DPPH] + k_2[P\cdot]^2 + 2k_4[P\cdot]\,[PO_2\cdot] +$$

$$k_5[PO_2\cdot]\ [DPPH]+k_6[PO_2\cdot]^2 \qquad\qquad (13)$$

At a higher DPPH concentration, the terms independent of [DPPH] are neglected with the assumption that most of the initial polymer radicals (P·) and peroxy radicals ($PO_2\cdot$) may be scavenged by DPPH. Eq. (14) is accordingly obtained.

$$G_pI=k_1[P\cdot]\ [DPPH]+k_5[PO_2\cdot]\ [DPPH] \qquad\qquad (14)$$

The rate of decrease in DPPH concentration is defined as

$$-d[DPPH]/dt=k_1[P\cdot]\ [DPPH]+k_5[PO_2\cdot]\ [DPPH] \qquad\qquad (15)$$

Eq. (16) is obtained from eqs. (14) and (15).

$$-d[DPPH]/dt=G_pI \qquad\qquad (16)$$

Consequently $\qquad\qquad [DPPH]=-G_pIt+[DPPH]_0 \qquad\qquad (17)$

At a lower DPPH concentration, the terms other than the last term of right-hand side of eq. (13) are neglected with the assumption that polymer radicals (P·) react with oxygen to give peroxy radicals immediately after their formation and most of the peroxy radicals react each other. Eqs. (18) and (19) are accordingly obtained.

$$G_pI=k_6[PO_2\cdot]^2 \qquad\qquad (18)$$

$$[PO_2\cdot]=(G_pI/k_6)^{1/2} \qquad\qquad (19)$$
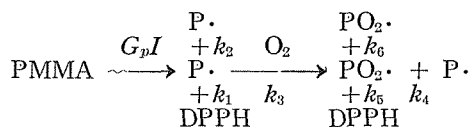
Thus the rate of decrease in DPPH concentration is

$$-d[DPPH]/dt=k_5(G_pI)^{1/2}[DPPH]/k_6^{1/2} \qquad\qquad (20)$$

Consequently $\qquad \ln[DPPH]=-k_5(G_pI)^{1/2}t/k_6^{1/2}+\ln[DPPH]_0 \qquad\qquad (21)$

At a higher DPPH concentration, the slope of the linear relation between the radical concentration and irradiation time corresponds to the value of $-G_pI$, which is the same value as *in vacuo*; at a lower DPPH concentration, the slope between the logarithm of radical concentration and irradiation time is $-k_5(G_pI)^{1/2}/k_6^{1/2}$.

Comparison of the rate constants of the elementary reactions

The elementary reactions described above are summarized as follows;

$$
\begin{array}{ccccc}
 & P\cdot & & PO_2\cdot & \\
 & G_pI \quad +k_2 & O_2 & +k_6 & \\
PMMA \;\rightsquigarrow & P\cdot \;\xrightarrow{\qquad} & & PO_2\cdot \;+\; P\cdot & \\
 & +k_1 \quad k_3 & & +k_5 \quad k_4 & \\
 & DPPH & & DPPH &
\end{array}
$$

The rate constants of these reactions are compared. From the slope of the linear relation at a higher initial concentration of DPPH, the relative values of G_pI are calculated to be 0.0029 and 0.0034 in the presence of air and *in vacuo*, respectively. From the slope at a lower initial concentration of DPPH, the values of $k_5(G_pI)^{1/2}/k_6^{1/2}$ and $k_1(G_pI)^{1/2}/k_2^{1/2}$ are 0.014 and 0.0025, respectively. And then the values of $k_5/k_6^{1/2}$ and $k_1/k_2^{1/2}$ are 0.26 and 0.0043, respectively. Consequently the value of $k_5/k_6^{1/2}$ is larger than that of $k_1/k_2^{1/2}$. ESR signal is obtained when PMMA is irradiated *in vacuo* but not in the presence of air in the present investigation. Therefore the rate constant k_2 seems to be much smaller than k_6 and then it is concluded that k_5 is much larger than k_1, namely,

the rate constant of the reaction of the peroxy radical ($PO_2\cdot$) with DPPH is much larger than that of the initial polymer radical ($P\cdot$) with DPPH.

Experiments are also carried out with polystyrene. It has been known that G value of the radical formation in polystyrene is 0.015, a very much smaller one than the value of 3 for PMMA. The rate of decrease in DPPH concentration is observed to be smaller than in the case of PMMA.

ACKNOWLEDGEMENT

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