

# Photolysis of Poly(3-Buten-2-One), Poly(4,4-Dimethyl-1-Penten-3-One), and Poly(3-Methyl-3-Buten-2-One) in the Presence of Oxygen

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## Synopsis

Photolysis of poly(3-buten-2-one) (PMVK), poly(4,4-dimethyl-1-penten-3-one) (PBVK), and poly(3-methyl-3-buten-2-one) (PMIK) were carried out in dioxane under oxygen or nitrogen bubbling. The main chain degradations of PBVK and PMIK were quenched and polymeric peroxides were produced. The heat treatment of the polymer irradiated in the presence of oxygen promoted the degradation. The photodegradation of PMVK was enhanced in the presence of oxygen.

## INTRODUCTION

Photodegradations of carbonyl polymers proceed both through Norrish type I and type II mechanisms. The type I reaction yields both alkyl and acylradicals. The type II reaction is  $\alpha$ - $\beta$  cleavage reaction via a 1,4-biradical intermediate. Since oxygen quenches the triplet state and traps the radicals, the main chain degradation of the carbonyl polymer may be depressed in the presence of oxygen. However, the type II reactions of 1-phenyl-1-pentanone and 4-methyl-1-phenyl-1-pentanone were reported to be enhanced in the presence of oxygen.<sup>1</sup>

The photodegradations of poly(4,4-dimethyl-1-penten-3-one) (PBVK)<sup>2</sup> and poly(3-methyl-3-buten-2-one) (PMIK)<sup>3-5</sup> were reported to proceed predominantly through the type I mechanism. Although the photolysis of poly(3-buten-2-one) (PMVK) was reported to occur both the type I and type II reactions at nearly same quantum yields, the main chain degradation proceeded only through the type II mechanism.<sup>6,7</sup> The photolysis of these three aliphatic carbonyl polymers and copolymers of styrene with 3-buten-2-one and 3-methyl-3-buten-2-one [P(St-co-MVK)-10 and P(St-co-MIK)-9] were carried out in the presence of oxygen for the course of the studies as the followings: (1) an effect of oxygen on the main chain degradation; (2) a formation of a peroxide (PO) from the intermediate radical, and (3) a dependence of the decomposition of the PO on the main chain degradation. The reactions of 3,3-dimethyl-2-butanone<sup>8</sup> and 2-hexanone<sup>9</sup> were reported to proceed through the type I and type II mechanisms, respectively. The photolysis of them were carried out under same experimental conditions for the comparison with the results of the polymer samples.

## EXPERIMENTAL

## Materials

PMVK, PBVK, PMIK, P(St-co-MVK)-10, and P(St-co-MIK)-9 were synthesized by the radical mechanism. The ketone units in the copolymers were determined to be 9.7 (MVK copolymer) and 8.6 (MIK copolymer) mol % by the absorption measurements at  $\lambda = 313$  nm [ $\epsilon_{313 \text{ nm}} = 1.56 \times 10^2$  (MVK copolymer) and  $1.88 \times 10^2$  (MIK copolymer)  $\text{dm}^2 \text{mol}^{-1}$ ]. Number average molecular weights ( $M_n$ ) of the polymers were determined to be  $1.2 \times 10^5$  (PBVK),  $8.9 \times 10$  (PMIK),  $2.4 \times 10^5$  (MVK copolymer), and  $1.7 \times 10^5$  (MIK copolymer) by means of the following equations:

$$\text{PBVK: } [\eta] = 1.32 \times 10^{-4} M_n^{0.72} \text{ in dioxane at } 303 \text{ K}^{10} \quad (1)$$

$$\text{PMIK: } [\eta] = 1.64 \times 10^{-4} M_n^{0.635} \text{ in dioxane at } 303 \text{ K}^5 \quad (2)$$

$$\text{St copolymer: } [\eta] = 9.53 \times 10^{-5} M_n^{0.744} \text{ in benzene at } 288 \text{ K}^{11} \quad (3)$$

where  $[\eta]$  is an intrinsic viscosity of the polymer solution. The molecular weight of PMVK was estimated to be ca.  $2 \times 10^5$  by means of the relation between  $M_n$  and  $[\eta]$  reported by Guillet and Norrish.<sup>6</sup>

3,3-Dimethyl-2-butanone (A) and 2-hexanone (B) were dried on hydrous sodium sulfate and distilled twice under nitrogen gas.

Dioxane was refluxed for 10 h with concd hydrochloric acid. After neutralization, dioxane was refluxed three times for 10 h on potassium hydroxide pellets. It was dried on calcium hydride and distilled twice under nitrogen stream.

## Irradiation

Polymer solutions ( $5 \text{ g dm}^{-3}$ ) were irradiated in Pylex test tubes under  $\text{O}_2$  or  $\text{N}_2$  bubbling (ca.  $1 \times 10^{-4} \text{ dm}^3 \text{ s}^{-1}$ ) at 303 K by using a 300 W high pressure Hg lamp. The irradiation of 313 nm light (for the main chain degradation) was carried out by using two filter solutions, described before.<sup>4</sup>

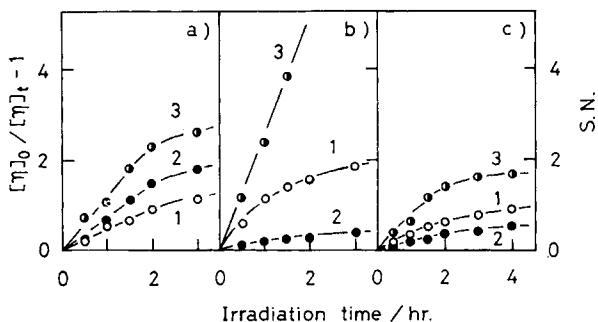


Fig. 1. Plots of S.N. or  $([\eta]_0/[\eta]_t - 1)$  (PMVK) vs. the irradiation time on the photodegradations of PMVK (a), PBVK (b), and PMIK (c) in dioxane by 313 nm irradiation. Polymer concentration =  $5 \text{ g dm}^{-3}$ ,  $I_{\text{abs}} = 6.7 \times 10^{-7} \text{ einstein dm}^{-3} \text{ s}^{-1}$ : (1) reaction under  $\text{N}_2$  bubbling; (2) reaction under  $\text{O}_2$  bubbling; (3) after the HT of the polymer solution under  $\text{O}_2$  bubbling.

Some of the solutions irradiated under O<sub>2</sub> bubbling were heated for 3 h at 353 K [heat treatment (HT)]. Scission number (S.N.) per macromolecular was determined by means of the change of the intrinsic viscosity of the polymer solution, described before.<sup>2,5</sup>

After the irradiation, peroxides (POs) or reductive products (RPs) in the solution were determined by means of iodometry.

IR measurements of the polymer samples were carried out as KBr disks by aids of a Perkin-Elmer IR-10 Type and a Nipponbunko A-202 Type.

DTA measurements of the polymer samples were carried out in argon gas by an aid of a RikagakuDenki TG-DTA Co-on Type (rate of the temperature rise:  $1.7 \times 10^{-1}$  deg s<sup>-1</sup>).

## RESULTS

### Main Chain Degradation

Photodegradations of PMVK, PVBK, PMIK, and the St copolymers by 313 nm irradiation were carried out in dioxane under O<sub>2</sub> or N<sub>2</sub> bubbling. Figure 1 shows the plots of S.N. vs. the irradiation time in the reactions of the homopolymers [ $([\eta]_0/[\eta]_t - 1)$  in PMVK]. An effect of oxygen gives by the ratio of the slopes in the presence and in the absence of O<sub>2</sub> in Figure 1 as  $r_1 (= \phi_{O_2}/\phi_{N_2})$ . The degradations of PBVK and PMIK, which proceeded through the type I mechanism, were quenched by oxygen [ $r_1 = 0.18$  (PBVK), 0.31 (PMIK)]. The main chain degradations of PMVK and the St copolymers, which proceeded through the type II mechanisms, were enhanced in the presence of O<sub>2</sub> rather than in its absence ( $r_1 = 1.17$  (PMVK), 1.48 [P(St-co-MVK)-10], and 1.52 [P(St-co-MIK)-9]).

In the presence of O<sub>2</sub>, the intermediate radical must be trapped and may produced a peroxide (PO). The decomposition of the PO may lead to the main chain scission. Figure 1 shows also the plot of S.N. after a heat treatment (HT, for 3 h at 353 K). The degradations of them were promoted effectively. The ratios of the slopes of S.N. after and before the HT,  $r_2 (= \phi_{O_2\Delta}/\phi_{O_2})$ , are 1.74, 11, and 1.54 for PMVK, PBVK, and PMIK, respectively.

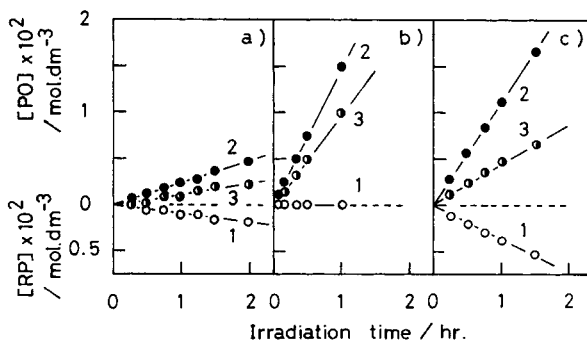


Fig. 2. Yields of the RP and the PO in the photolysis of PMVK (a), PBVK (b), and PMIK (c) in the dioxane by the irradiation ( $\lambda_{irr} = 300$  nm): (1) formation of the RP in the reaction under N<sub>2</sub> bubbling; (2) formation of the PO in the reaction under O<sub>2</sub> bubbling; (3) yield of the PO after the HT.

### Formation of Peroxide

The POs were produced by the irradiations of PMVK, PBVK, and PMIK under O<sub>2</sub> bubbling. In the reaction of PMVK and PMIK under N<sub>2</sub> bubbling, reductive products (RPs) were detected. In the photolysis of the copolymer with MVK the RP and the PO could not be detected. Figure 2 shows the yields of the PO and the RP determined by means of iodometry ( $\lambda_{\text{irr}} \geq 300$  nm).

The photolysis of these polymers yield polymer radicals and fragment radicals. The determinations of the PO and the RP were carried out before and after the precipitation of the polymer from the solution. The POs were produced both from the radicals nearly equivalently. The RPs in the reactions of PMVK and PMIK were produced only the fragment radicals.  $\alpha$ -Cleavage reactions of PMVK<sup>6</sup> and PMIK<sup>3</sup> were reported to yield acetyl radical to produce ethanal. The RP can be concluded to be ethanal. The photolysis of PBVK under N<sub>2</sub> bubbling did not produce the RP.  $\alpha$ -Cleavage reaction of PBVK was reported to yield polymeric acylradical and *tert*-butyl radical.<sup>2</sup> The polymeric acylradical decomposed easily to secondary polymer radical and carbon monoxide.<sup>2</sup> By the addition of 1-pentanethiol (2 mol dm<sup>-3</sup>), the RP was produced from the polymer radical. The RP in PBVK seems to be formyl group in the polymer chain.

### Reaction of Model Compound

Photolysis of 3,3-dimethyl-2-butanone (A) and 2-hexanone (B) were carried out under same experimental conditions as the reactions of the polymer samples ( $\lambda_{\text{irr}} = 300$  nm). The formations of the type I reaction product of A, 2-methyl-2-propene (C) and ethanal (D), were depressed by oxygen, although the formation of the type II reaction product of B, propanone (E), was enhanced. The effect of oxygen,  $r_1 =$  the ratio of the relative yields, were 0.10, 0.22, and 1.35 for C, D, and E, respectively. The photolysis of A produced the POs and the RPs depending on experimental conditions. However, they were not detected in the photolysis of B as the results of the copolymers.

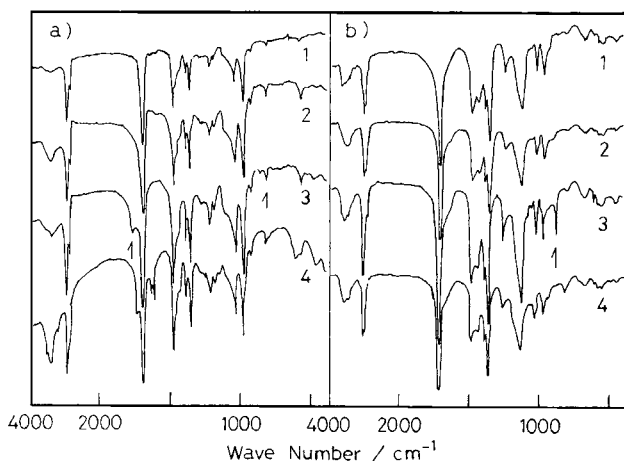


Fig. 3. Changes of IR spectra of PBVK (a) and PMIK (b) in the irradiation. Polymer concentration: 5 g dm<sup>-3</sup> in dioxane: (1) before the reaction; (2) after the reaction under N<sub>2</sub> bubbling, (3) after the reaction under O<sub>2</sub> bubbling, (4) after the HT of the polymers irradiated under O<sub>2</sub> bubbling.

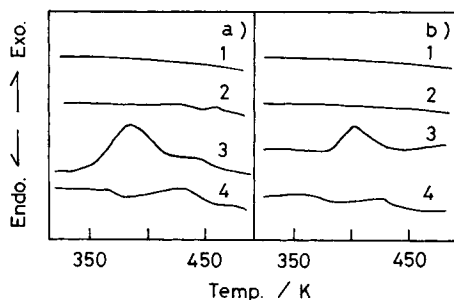


Fig. 4. Changes of DTA curves of PBVK (a) and PMIK (b) in the irradiation: (1) before the reaction; (2) after the irradiation under  $N_2$  bubbling; (3) after the reaction under  $O_2$  bubbling; (4) after the HT of the polymers irradiated under  $O_2$  bubbling.

### Change of IR Spectrum by the Irradiation

Figure 3 shows IR spectra of PBVK and PMIK before and after the irradiation in dioxane under  $O_2$  or  $N_2$  bubbling. The spectra after the HT are also shown in this figure.

The IR spectrum of PBVK reacted in the absence of  $O_2$  shows the formation of olefins evidenced by the appearance to the peaks at  $1660\text{ cm}^{-1}$  ( $\nu_{C=C}$ ) and  $912\text{ cm}^{-1}$  ( $\delta_{CH\text{ op, olefin}}$ ). After the reaction under  $O_2$  bubbling, the peaks of the PO were appeared at  $3580\text{ cm}^{-1}$  ( $\nu_{O-H, -O_2H}$ ),  $1780\text{ cm}^{-1}$  ( $\nu_{C=O, -CO_2H}$ ),  $1100\text{ cm}^{-1}$  ( $\nu_{C-O}$ ), and  $870\text{ cm}^{-1}$  ( $\nu_{O-O}$ ). By the HT, the peaks due to the PO were disappeared, and the peaks assigned both to carboxy group and the olefin were measured at  $1738\text{ cm}^{-1}$  ( $\nu_{C=O, -CO_2R}$ ) and  $1620\text{ cm}^{-1}$  ( $\nu_{C=C}$ ).

In the reaction of PMIK under  $N_2$  bubbling, typical changes of the IR spectrum could not be detected. PMIK reacted under  $O_2$  bubbling exhibits the peaks at ca.  $3600\text{ cm}^{-1}$  ( $\nu_{O-H}$ ),  $890$  and  $875\text{ cm}^{-1}$  ( $\nu_{O-O}$ ), which were ascribable to the PO. By HT, the peaks assigned to the olefin were appeared at  $1640\text{ cm}^{-1}$  ( $\nu_{C=C}$ ) and  $805\text{ cm}^{-1}$  ( $\nu_{CH\text{ op, olefin}}$ ).

### DTA Measurement of the Irradiated Polymer

Figure 4 shows DTA curves of PBVK and PMIK before and after the irradiation under  $N_2$  or  $O_2$  bubbling in dioxane. The samples before and after the reaction in the absence of  $O_2$  did not exhibit exothermic peaks. After the irradiation under  $O_2$  bubbling, the polymers exhibited the exothermic peaks at  $383\text{ K}$  and (a minor peak) at  $423\text{ K}$  (PBVK) and  $403\text{ K}$  (PMIK). By the HT of them, the peaks of PBVK at  $383\text{ K}$  and of PMIK were disappeared. It means that the peaks due to the POs.

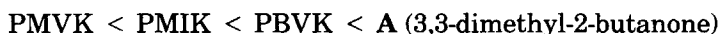
### DISCUSSION

Oxygen quenches the triplet state and traps the radical intermediates. Since the triplet lifetime ( $\tau_T$ ) of PMVK has been reported to be  $6\text{ ns}$ ,<sup>12</sup> and  $\tau_T$  of PBVK and PMIK are estimated to be shorter than  $3\text{ ns}$ ,\* the triplet quenching by oxygen is not the most important deactivating process.

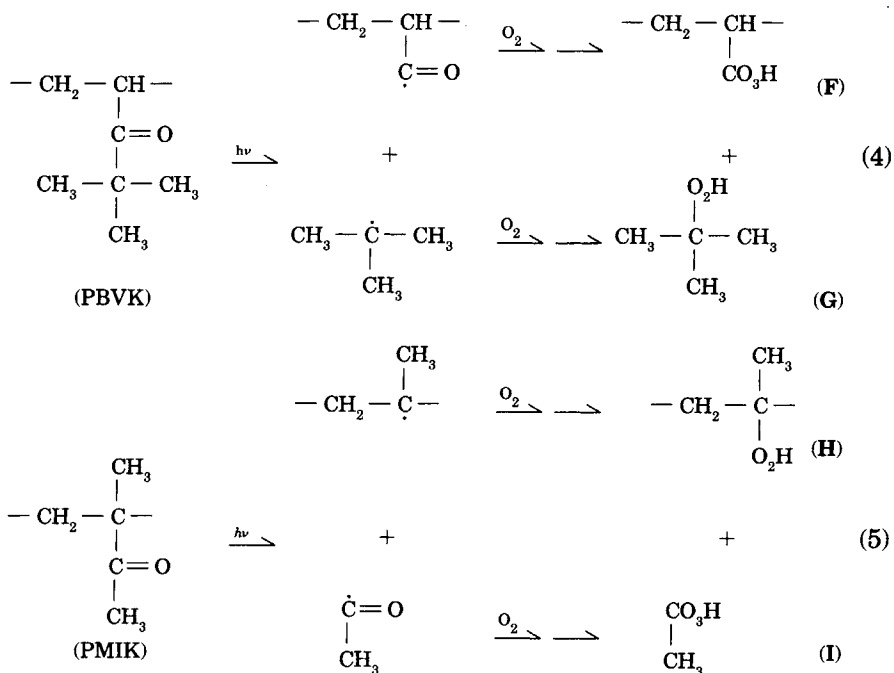
The photodegradations of PBVK and PMIK in the presence of  $O_2$  were quenched, and the POs were produced at good yields. The quantum yields

\* The  $\tau_T$  and  $kq\tau_T$  of PMVK were reported in Ref. 12. The  $\tau_T$  of PBVK and PMIK were estimated by means of  $kq\tau_T$  [=  $16$  (PMVK),<sup>12</sup>  $7.1$  (PBVK),<sup>2</sup> and  $4.9$  (PMIK)<sup>5</sup>  $\text{dm}^3\text{ mol}^{-1}$  by using of *cis*, *cis*-1,3-cyclooctadiene as a quencher].

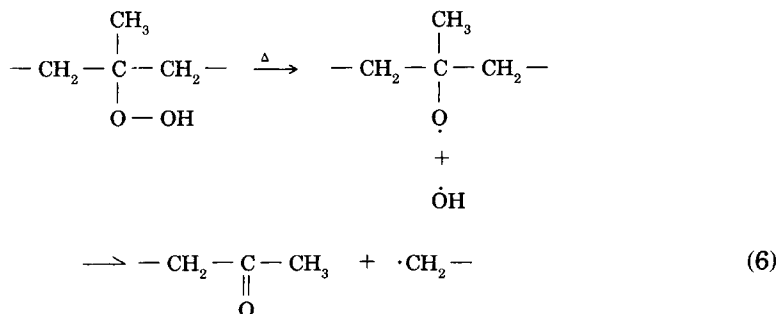
of the  $\alpha$ -cleavage reaction were reported to be 0.03 (PMVK),<sup>6</sup> 0.5 (PBVK),<sup>13</sup> 0.3 (PMIK)<sup>13</sup> and 0.8 (A).<sup>14</sup> The order of the yield of the PO agrees with the order of  $\phi_{\alpha}$ , as follows:



The  $\alpha$ -cleavage reaction of the polymer sample yields the polymer radical and the fragment radical. The polymer PO and the low molecular PO were produced nearly equivalently. The structures of the polymer POs produced from PBVK and PMIK were identified as peroxycarboxylic acid (F) and hydroperoxide (H), respectively. It can be concluded that the POs are produced by the additions of oxygen with the  $\alpha$ -cleaved radicals, as follows [eqs. (4), PBVK, and (5), PMIK]:

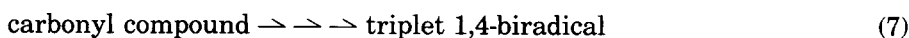


The decomposition of the polymer PO led to the main chain degradation. The polymer PO from PMIK should degrade as same the mechanism to the PO of poly(propene)<sup>15</sup> reported as

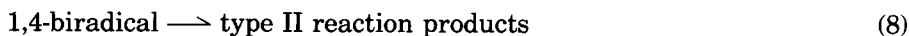


The ratio  $r_2$  of PBVK is too high as 11. Then, the degradation of this polymer seems to be caused not only by the polymer PO but the low molecular PO (G).

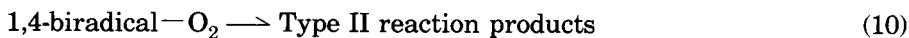
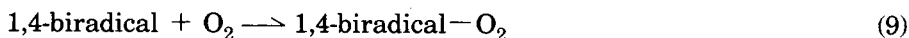
The main chain degradations of PMVK and the St copolymers and the reaction of 2-hexanone were enhanced in the presence of  $O_2$ . In the  $O_2$  saturated solution, the most important process of the decay of the triplet 1,4-biradical was oxygen trapping.<sup>16</sup> The yield of the type II reaction product on the aliphatic carbonyl compound should be higher from the adduct of oxygen with the 1,4-biradical than from the beared 1,4-biradical as the results of the aromatic carbonyl compounds reported.<sup>1</sup> The PO could not be detected in the reactions of the copolymer with MVK and 2-hexanone. It seems that oxygen added reforms at  $\alpha$ - $\beta$  cleavage reaction. Then, the reaction can be written as the follows:



(in the absence of  $O_2$ )



(in the presence of  $O_2$ )



### CONCLUSION

In the presence of  $O_2$ , the main chain degradations of PBVK and PMIK, which proceeded through the type I mechanism, were quenched and the POs were produced at good yields. It seems the photolysis of them under  $O_2$  are the easiest method to synthesize the polymer POs (peroxycarboxylic acid and hydroperoxide). By the HT of the polymer PO, the main chain degradation was promoted.

The type II reaction of the aliphatic carbonyl compounds was enhanced in the presence of  $O_2$ . It is the lack of the results for drawing the conclusion but it seems that the adduct of oxygen with the 1,4-biradical intermediate is difficult to reform the starting material.

We are grateful for Professor E. Imoto of our university, Assistant Professor K. Horie of University of Tokyo, and Assistant Professor S. Kojiya of Kyoto Technical University for useful discussions.

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Received July 20, 1983

Accepted March 5, 1984