Photodegradation of Polypropylene in the Presence of Ferric Chloride

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Synopsis

The effect of ferric chloride (FeCl$_3$) on photodegradation of isotactic polypropylene (PP) was investigated using mainly ESR spectrometry. PP powder, its oxidized samples, and FeCl$_3$-adsorbing PP samples were irradiated under a nitrogen atmosphere at 77°K with ultraviolet light from a high-pressure mercury lamp and a superhigh-pressure mercury lamp modified by various filters. Methyl, polymerci alkyl, and peroxy radicals were observed in the ESR spectra of the irradiated samples, and it was found that FeCl$_3$ depresses the formation of alkyl radicals and accelerates the formation of peroxy radicals catalyzing the reaction. From infrared study of UV-irradiated film samples, it was also inferred that FeCl$_3$ accelerates the photodegradation the hydroperoxide and carbonyl groups.

INTRODUCTION

ESR studies of photodegradation of polypropylene (PP) have been reported by several authors.[1-4] As PP has no definite absorption of UV at wavelengths longer than 200 nm,[5] photodegradation of PP is thought to be initiated from various sites in the samples including trace amount of metal impurities,[6-9] oxidized groups such as hydroperoxide[10,11] and carbonyl, unsaturated double bonds,[12] and so on. However, the mechanism of the degradation process of PP seems to be too complicated to be revealed sufficiently.

We have already reported[13] the sensitizing effect of ferric chloride (FeCl$_3$) on the photodegradation of cellulose and related polymers, so it is interesting to learn further its effect on the photodegradation of nonpolar polymers.

Ferric salt-sensitized photodegradation of polyolefins[8,14,15] has been reported, and it was also suggested that FeCl$_3$ affects the photodegradation of polyethylene emphasizing the Norrish-type II reaction at carbonyl groups. In addition, a redox-type catalytic decomposition of peroxide was reported,[16] which led to an appreciable increase of peroxy radical concentration.

In the present paper, the effect of FeCl$_3$ on the photodegradation of PP was investigated in more detail, and the photodegradation mechanisms of PP were also touched upon.

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EXPERIMENTAL

Sample

Isotactic PP used for the photodegradation tests was neat powder finer than 60 mesh with weight-average molecular weight of about 14.54×10^4. Oxidized samples were prepared by irradiating the PP powder for 3 hr at ambient temperature in air with light from a high-pressure mercury lamp. Reagent-grade $FeCl_3 \cdot 6H_2O$ was used without further purification. $FeCl_3$-adsorbing samples were prepared by immersing nonoxidized or oxidized PP powder for 60 min at 45°C in acetone solution of $FeCl_3$ of a known concentration and drying under vacuum. The amount of adsorbed $FeCl_3$ was determined by iodometric titration.

Irradiation and ESR Measurement

About 0.30 g PP sample was placed in a quartz glass tube about 5 mm in diameter for measurement of ESR spectrum, which was evacuated after substitution with nitrogen gas. The PP sample after irradiation in the tube at 77°K in a Dewar flask was set in the ESR instrument for the measurement of the spectrum, the cavity of which was kept at 77°K. A Toshiba high-pressure mercury lamp H 400-P and a Ushio superhigh-pressure mercury lamp 250-D were used as light sources. During the irradiation, several kinds of color filters (Toshiba glass filter) were used to select the light wavelength. The ESR measurements of the irradiated samples were made with a Japan Electron Optics Laboratory JES-ME-X. Resonance spectra were observed with x-band and 100 kcps field modulation. Blank test confirmed that no effect of acetone still remaining in the sample was detectable in the experiment.

Infrared Measurement

PP film samples about 0.20 ± 0.02 mm thick were prepared by rapid quenching after pressing the PP powder at 170°C under vacuum. The film samples were irradiated in the quartz glass tube at room temperature under nitrogen or air atmosphere, followed by the infrared measurement using a Hitachi EPI-G3 instrument.

RESULTS

Irradiation with High-Pressure Mercury Lamp Under Nitrogen

ESR spectra of the PP samples irradiated at 77°K for 60 min under nitrogen atmosphere are shown in Figure 1. $FeCl_3$-free PP samples showed spectra containing sharp and broad quartets. The sharp quartet spectrum with a splitting constant of about 22 gauss was unstable at 77°K, and the signal intensity decreased appreciably at the temperature. This spectrum could be attributed to methyl radicals.[1-3] The broad quarted showed a splitting constant of about 24 gauss and was more stable at 77°K, which was supposed to correspond to alkyl radical, $—CH_2—CH(\dot{C}H_2)—CH_2—$.[17-19] The spectrum shape of $FeCl_3$-ab-
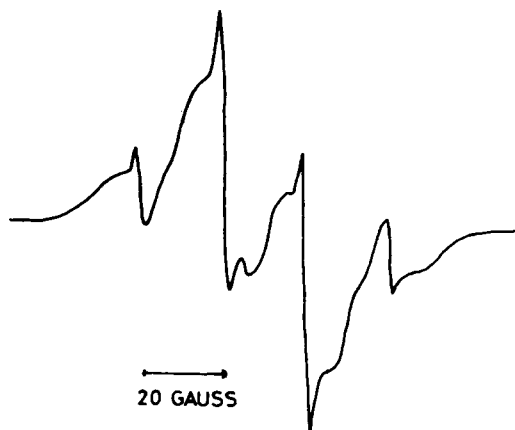
Fig. 1. ESR spectrum of PP. Light, high-pressure mercury lamp ($\lambda > 220$ nm); time, 60 min; temperature, 77°K; atmosphere, nitrogen.

sorbing PP sample closely resembled to that of $FeCl_3$-free PP sample, but a somewhat lower signal intensity was observed.

Dependence of the relative signal intensity on the $FeCl_3$ concentration is shown in Figure 2. Since the signal intensity decreased with increase in the $FeCl_3$ concentration, it may be assumed that $FeCl_3$ contributes to suppress the formation of the alkyl radicals under photoirradiation.

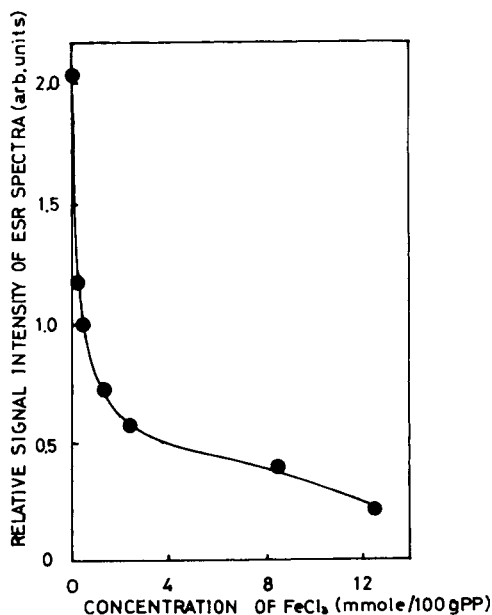
Fig. 2. Relationship between ESR signal intensity of irradiated PP and $FeCl_3$ concentration. Time, 60 min; temperature, 77°K; wavelength of light λ, > 220 nm; atmosphere, nitrogen.

Irradiation with Light Passed Through a Pyrex Filter

The signal intensity of PP samples in the irradiation system with light filtered by a Pyrex glass ($\lambda > 300$ nm) was too weak to estimate the radical species. On the other hand, an asymmetric line was present in the spectra given for $FeCl_3$-adsorbing samples, as shown in Figure 3, which was assigned to peroxy radical, ROO·.[19-21] No change in the line shape was observed relating to the amount of $FeCl_3$ adsorbed in the sample, while absorption maximum of signal intensity was shown at $FeCl_3$ amount of 1.3 mmole/100 g PP. Such an effect to suppress the formation of peroxy radicals in the range of high $FeCl_3$ levels seems to be caused by the self-filtration effect of $FeCl_3$.

Irradiation with Light Passed Through Color Filters

$FeCl_3$-free and $FeCl_3$-adsorbing PP samples were irradiated at 77°K with light from the superhigh-pressure mercury lamp passed through a series of color glass filters as follows: UV-29 ($\lambda > 260$ nm), UV-31 ($\lambda > 265$ nm), UV-35 ($\lambda > 335$ nm), and VY-42 ($\lambda > 370$ nm). ERS spectra were measured at 77°K. The spectra are shown in Figure 4. When the PP sample was irradiated using a UV-29 filter, mainly a broad quartet, $-CH_2-CH(\dot{C}H_2)-CH_2-$, was observed, as shown in Figure 4(b), in which any sharp quartet component was hardly detected. When a UV-31 filter was used, a broad quartet spectrum including a weak singlet component was observed in the central position of the spectrum. The spectrum seems to be that from alkoxy radical.

A weak asymmetric line was given by the UV-35 filter. Using the VY-42 filter, no ESR signal was recorded. By adsorbing of $FeCl_3$ on PP, the signal intensity of the irradiated sample was noted to decrease. However, it was interesting to find an asymmetric singal (peroxy radical) in the case of irradiation through glass filters. It seems that peroxide groups or a very minor amount of oxygen molecules remaining in the PP samples can be the oxygen source for peroxy radicals in this reaction.

By using UV-29 and UV-31 filters, the effect of $FeCl_3$ on the signal intensity
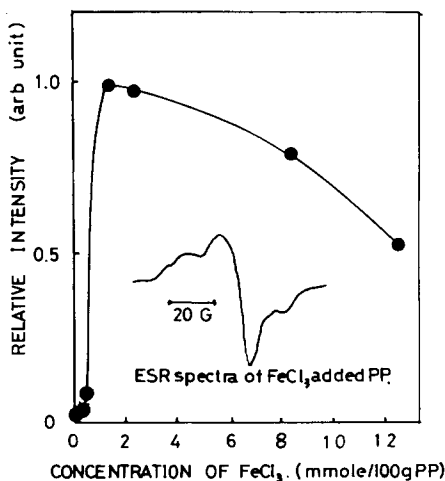

Fig. 3. Change of ESR signal intensity of irradiated PP with $FeCl_3$ concentration and ESR spectra of PP with $FeCl_3$. Time, 60 min; light, superhigh-pressure mercury lamp; filter, Pyrex glass ($\lambda > 300$ nm); temperature, 77°K; atmosphere, nitrogen.
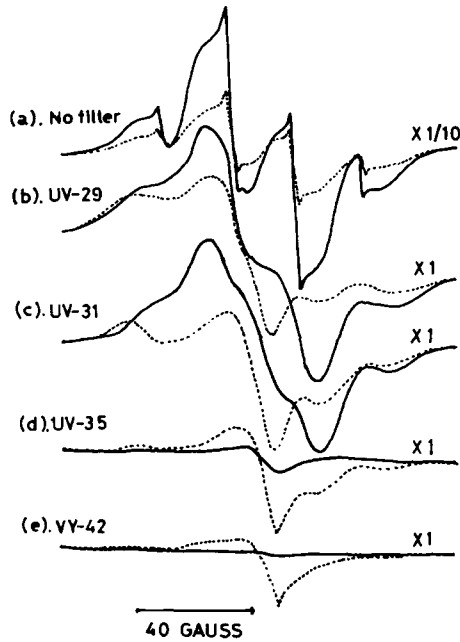
Fig. 4. Wavelength dependence of radical formation in PP (—) and PP with $FeCl_3$ (1.3 mmole/100 g PP) added (- - -). Time, 60 min; light, superhigh-pressure mercury lamp; filters, no filter ($\lambda >$ 220 nm) (a), UV-29 ($\lambda >$ 260 nm) (b), UV-31 ($\lambda >$ 265 nm) (c), UV-35 ($\lambda >$ 335 nm) (d), UV-42 ($\lambda >$ 370 nm) (e); temperature, 77°K; atmosphere, nitrogen.

was known to be suppression.   However, a contrary tendency was observed with UV-35 and VY-42 filters.   The same effect of $FeCl_3$ is also suggested in Figure 5, which shows the change in signal intensities with irradiation time using UV-29 and UV-35 filters.
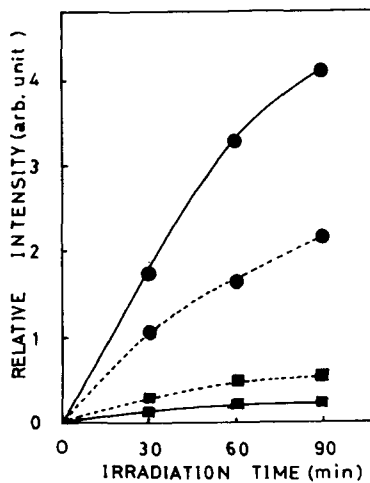

Fig. 5. Wavelength dependence of ESR signal intensity of irradiated PP (—) and PP with $FeCl_3$ (1.3 mmole/100 g PP) added (- - -).   Light, superhigh-pressure mercury lamp; filters, UV-29 (●), UV-35 (■); temperature, 77°K; atmosphere, nitrogen.

Irradiation of Oxidized PP Sample

Oxidized PP samples were irradiated with the light from the high-pressure mercury lamp under nitrogen atmosphere, and the ESR spectra of samples after heat treatment are shown in Figure 6. The line shape shows the presence of alkyl radicals in the sample after 144°K treatment and an asymmetric spectrum, peroxy radicals, in the samples after 177° and 219°K treatments. Thus, it was noted that the irradiation-oxidized PP samples include peroxy radical, ROO·, which is hardly observed in an ESR spectrum of nonoxidized sample.

Irradiations for $FeCl_3$-adsorbing oxidized PP sample using various filters were carried out. Figure 7 shows a series of the ESR spectra of the samples with wavelength of light, and Figure 8 shows the relationship between relative signal intensity and irradiation time for each sample. The figures suggest that $FeCl_3$ depresses the formation of alkyl radical in the irradiation with light of shorter wavelength, while it accelerates the formation of peroxy radical with light of longer wavelength.

Infrared Study

Infrared spectra of $FeCl_3$-free and $FeCl_3$-adsorbing PP film samples irradiated with light from the high-pressure mercury lamp in air at ambient temperature were measured. The changes in the relative absorbance at 3400 cm^{-1} (—OOH),[22–24] 1715 cm^{-1} (>C=O),[24–26] and 1640 cm^{-1} (>C=C<)[10] with irradiation time are shown in Figures 9 and 10. The absorbance at 3400 cm^{-1} markedly increased on increasing the amount of absorbed $FeCl_3$. The absorbance at 1715 cm^{-1} showed a maximum value at a certain amount of $FeCl_3$, and the existence of an optimum amount of $FeCl_3$ for the formation of carbonyl group was suggested. The increase in the absorbance at 1640 cm^{-1} for irradiated samples was clearly restrained as the amount of $FeCl_3$ increased, which means that $FeCl_3$ affects to suppress the formation of ethylenic double bond.
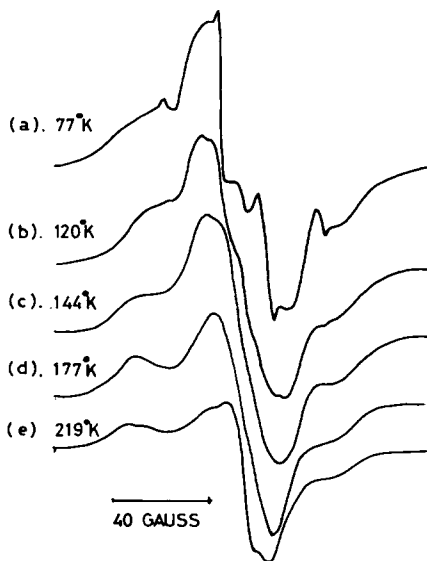

Fig. 6. ESR spectra of oxidized PP irradiated with high-pressure mercury lamp at 77°K in nitrogen atmosphere: (a) observed immediately at 77°K after irradiation; (b), (c), (d), and (e) observed at 77°K after heat treatment of (a) at indicated temperatures for 1 min.
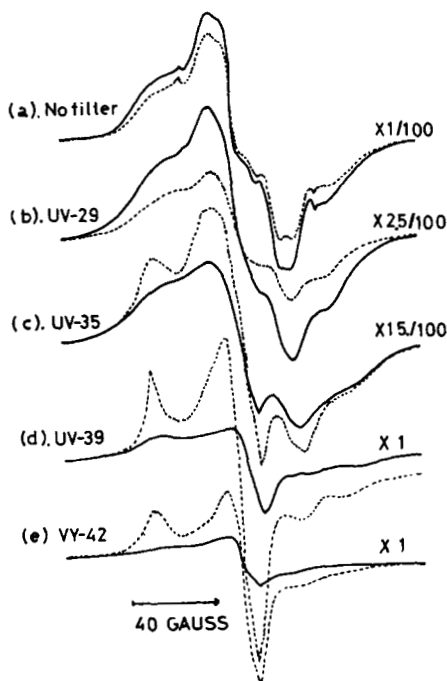
Fig. 7. Wavelength dependence of radical formation in oxidized PP (—) and oxidized PP with FeCl$_3$ (1.2 mmole/100 g PP) added (- - -). Time, 60 min; light, superhigh-pressure mercury lamp; filters, no filter (λ > 220 nm) (a), UV-29 (λ > 260 nm) (b), UV-35 (λ > 335 nm) (c), UV-39 (λ > 365 nm), (d) VY-42 (λ > 370 nm) (e); temperature, 77°K; atmosphere, nitrogen.
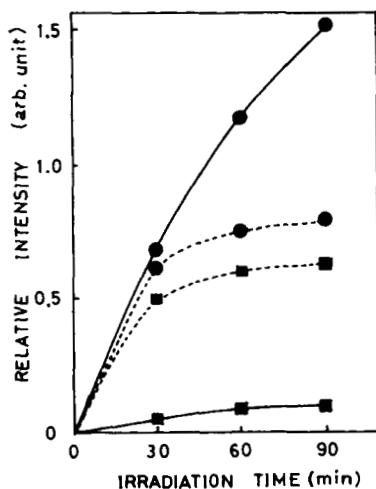
Fig. 8. Wavelength dependence of ESR signal intensity of irradiated oxidized PP (—) and oxidized PP with FeCl$_3$ (1.2 mmole/100 g PP) added (- - -). Light, superhigh-pressure mercury lamp; filters, UV-29 (●), UV-35 (■); temperature, 77°K; atmosphere, nitrogen.

Oxidized PP samples decreased in absorbance at 3400 and 1715 cm^{-1} with irradiation under nitrogen atmosphere, which means that the photodegradation of hydroperoxide and carbonyl groups took place in the sample. These phe-
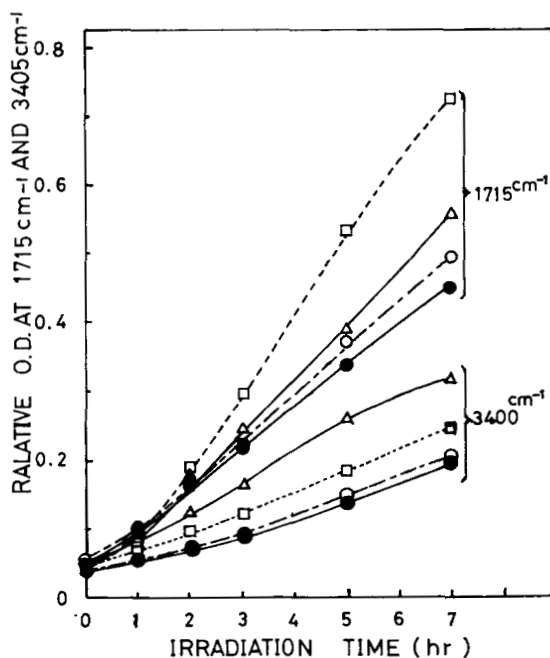
Fig. 9. Effects of FeCl₃ on IR absorption at 1715 cm⁻¹ (>C=O) and 3400 cm⁻¹ (—OH) in PP films (0.20 mm) irradiated with high-pressure mercury lamp in air at ambient temperature. Concentration of adsorbed FeCl₃: (●) 0; (○) 0.16 mmole/100 g PP; (□) 2.33 mmole/100 g PP; (△) 8.40 mmole/100 g PP.
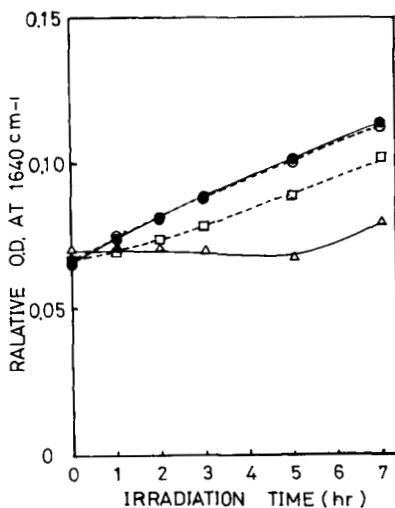
Fig. 10. Effects of FeCl₃ on IR absorption at 1640 cm⁻¹ (>C=C<) in PP films (0.20 mm) irradiated with high-pressure mercury lamp in air at ambient temperature. Concentration of adsorbed FeCl₃: (●) 0; (○) 0.16 mmole/100 g PP; (□) 2.33 mmole/100 g PP; (△) 8.40 mmole/100 g PP.

nomena can be interpreted by the cleavage reaction of the polymer chains. As mentioned above, it is true that FeCl₃ accelerates the photodegradation of hydroperoxide and carbonyl groups and suppresses the formation of alkyl radicals.

DISCUSSION

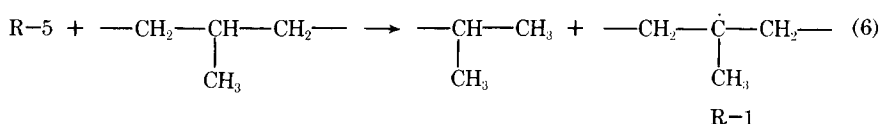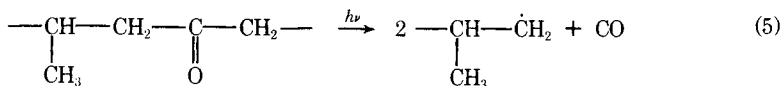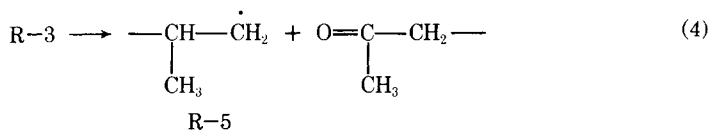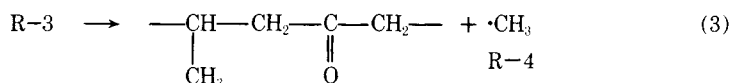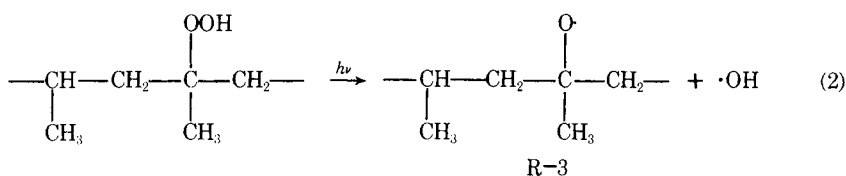ESR studies on radicals of UV-irradiated PP have hitherto been reported by several authors.[1-4] Rånby and Yoshida[1] reported that methyl and polymeric alkyl radicals were noticed in irradiated PP. A similar fact was also observed by Browning et al.[3] Tsjui and Seiki[2] reported that the radical once formed by irradiation can easily be changed into the other radical according to eq. (1) giving a broad four-line spectrum, which was confirmed by Loy[17] and Iwasaki et al.[18]

$$-CH_2-\dot{C}(CH_3)-CH_2- \xrightarrow{h\nu} -CH_2-CH(\dot{C}H_2)-CH_2- \qquad (1)$$
$$\text{R-1} \qquad\qquad\qquad \text{R-2}$$
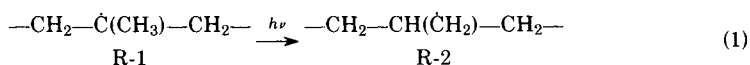
The broad four-line spectrum observed in the present study seems to be that the R-2 radical.

The weak singlet (g = 2.004) was observed at the central position of the spectrum of the irradiated sample with light passing through the UV-31 filter. The spectrum seems to be that from alkoxy radicals. It is said that the distinction between alkoxy and peroxy radical in terms of ESR spectrum is not easy,[27,28] however, the g value and the shape of the spectrum strongly support the above estimation.

The asymmetric spectrum observed in PP samples irradiated with light passing through the UV-35 filter is inferred to be that from peroxy radical. In the case of initiation at hydroperoxide group, the photodegradation scheme of PP can be explained by the following:

$$-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OOH}{|}}{C}}-CH_2- \xrightarrow{h\nu} -\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{O\cdot}{|}}{C}}-CH_2- + \cdot OH \qquad (2)$$
$$\text{R-3}$$

$$R-3 \longrightarrow -\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\overset{||}{O}}{C}-CH_2- + \cdot CH_3 \qquad (3)$$
$$\text{R-4}$$

$$R-3 \longrightarrow -\underset{\underset{CH_3}{|}}{CH}-\overset{\cdot}{C}H_2 + O{=}\underset{\underset{CH_3}{|}}{C}-CH_2- \qquad (4)$$
$$\text{R-5}$$

$$-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\overset{||}{O}}{C}-CH_2- \xrightarrow{h\nu} 2 -\underset{\underset{CH_3}{|}}{CH}-\dot{C}H_2 + CO \qquad (5)$$

$$R-5 + -CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2- \longrightarrow -\underset{\underset{CH_3}{|}}{CH}-CH_3 + -CH_2-\underset{\underset{CH_3}{|}}{\overset{\cdot}{C}}-CH_2- \qquad (6)$$
$$\text{R-1}$$

The formation of the peroxy radical may be possible by the next induced de-

composition, eq. (7)[10]:

$$
\begin{array}{c}
\text{O·} \qquad\qquad\qquad \text{OOH} \\
| \qquad\qquad\qquad\quad | \\
-\text{CH}-\text{CH}_2-\text{C}-\text{CH}_2- \;+\; -\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2- \\
| \qquad\quad | \qquad\qquad\qquad | \qquad\quad | \\
\text{CH}_3 \qquad \text{CH}_3 \qquad\qquad\qquad \text{CH}_3 \quad \text{CH}_3 \\
\text{R-3}
\end{array}
$$

$$
\begin{array}{c}
\text{OH} \qquad\qquad\qquad\qquad \text{OO·} \\
| \qquad\qquad\qquad\qquad\quad | \\
\longrightarrow \; -\text{CH}-\text{CH}_2-\text{C}-\text{CH}_2- \;+\; -\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2- \quad (7) \\
| \qquad\quad | \qquad\qquad\qquad\quad | \qquad\quad | \\
\text{CH}_3 \qquad \text{CH}_3 \qquad\qquad\qquad \text{CH}_3 \quad \text{CH}_3 \\
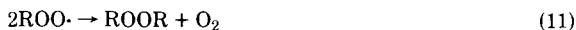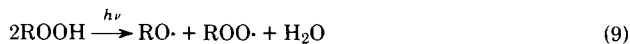\text{R-6}
\end{array}
$$
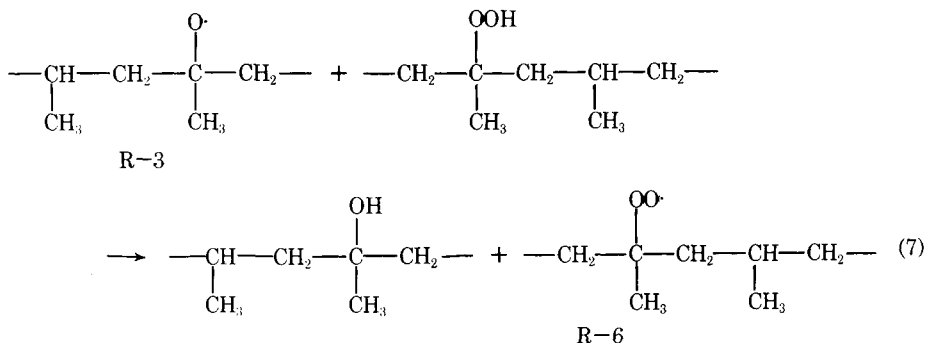
It is naturally considered that the active peroxy radicals abstract the adjacent hydrogen on tertiary carbon to form alkyl radical and hydroperoxide according to eq. (8):
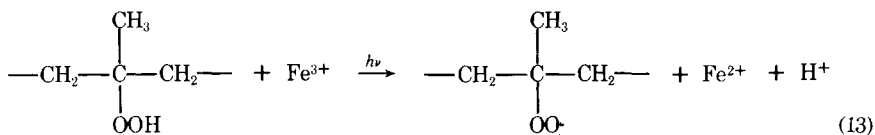
$$
\begin{array}{c}
\text{OOH} \\
| \\
\text{R-6} \;\longrightarrow\; -\text{CH}_2-\text{C}-\text{CH}_2-\dot{\text{C}}-\text{CH}_2- \qquad\qquad (8) \\
| \qquad\qquad | \\
\text{CH}_3 \qquad\quad \text{CH}_3
\end{array}
$$
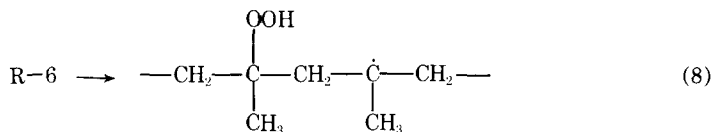
Photodegradation of Oxidized PP Samples

Oxidized PP samples show absorption of the infrared spectrum at $3400\ \text{cm}^{-1}$, which means the presence of a hydroperoxide group. The group is known to be easily photodegraded to form alkoxy and hydroxy radicals. Since the signal of peroxy radical rather than that of alkoxy radical was indicated in the present study, reactions of photodegradation of oxidized samples were estimated according to eqs. (9)–(12)[23,29–31]:

$$2\text{ROOH} \xrightarrow{h\nu} \text{RO·} + \text{ROO·} + \text{H}_2\text{O} \qquad (9)$$

$$\text{RO· (or ROO·)} + \text{RH} \rightarrow \text{ROH (or ROOH)} + \text{R·} \qquad (10)$$

$$2\text{ROO·} \rightarrow \text{ROOR} + \text{O}_2 \qquad (11)$$

$$\text{R·} + \text{O}_2 \rightarrow \text{ROO·} \qquad (12)$$

It was clearly recognized that FeCl_3 acts to suppress the formation of alkyl radicals under irradiation with light including shorter wavelengths with either nonoxidized or oxidized samples.

On the other hand, FeCl_3 emphasized the formation of peroxy radical in the case of irradiation with light of longer wavelenths. This effect of FeCl_3 was shown more distinctly for oxidized PP samples, and was also supported by infrared study. The effect is believed to originate in the hydrogen-abstracting reaction due to redox mechanism between ferric ion and the hydroperoxide group, as shown in eq. (13):

$$
\begin{array}{c}
\text{CH}_3 \qquad\qquad\qquad\qquad\qquad\qquad \text{CH}_3 \\
| \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\
-\text{CH}_2-\text{C}-\text{CH}_2- \;+\; \text{Fe}^{3+} \xrightarrow{h\nu} \; -\text{CH}_2-\text{C}-\text{CH}_2- \;+\; \text{Fe}^{2+} \;+\; \text{H}^+ \\
| \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\
\text{OOH} \qquad\qquad\qquad\qquad\qquad\qquad \text{OO·} \qquad\qquad\qquad (13)
\end{array}
$$

Besides the effect of $FeCl_3$ based on a direct energy transfer mechanism, the effect of the $Fe^{3+}OH^-$ state leading to the following equations should also be considered, because a part of $FeCl_3$ in the reaction system might be changed into the $Fe^{3+}OH^-$ state, where a small amount of ROOH is contained as a component of the sample:

$$Fe^{3+}OH^- \xrightarrow{h\nu} Fe^{2+} + \cdot OH \tag{14}$$

$$ROOH + \cdot OH \rightarrow ROO\cdot + H_2O \tag{15}$$

In conclusion, it is true to state that $FeCl_3$ essentially participates in the photodegradation of the PP to accelerate the degradating reactions of carbonyl and hydroperoxy group in the samples.

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