ESR Study of the Effect of Ferric Chloride on the Photodegradation of Model Compound for Polypropylene

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Synopsis

In our previous article on the photodegradation of polypropylene (PP), the effects of ferric chloride (FeCl$_3$) accelerating the formation of peroxy radical and depressing the formation of alkyl radical were reported. In the present article, the influence of FeCl$_3$ on model compounds of PP was examined using electron spin resonance (ESR) spectrometry. The following compounds were employed as models of PP, including its irregular structures: 2-methylpentane (2-MP), 2,4-dimethylpentane (2,4-DMP), 2-methyl-4-pentanone (2-M4P), 2,6-dimethyl-4-heptanone (2,6-DM4H), 2-methyl-1-pentene (2-M1P), and *tert*-butylhydroperoxide (*t*-BuO$_2$H). FeCl$_3$ accelerated the formation of alkyl radicals for 2-MP and 2,4-DMP, alkyl and acyl radicals for 2-M4P and 2,6-DM4H, and alkyl radicals for 2-M1P. As no definite effect of FeCl$_3$ was observed for *n*-pentane and 2-octanone, FeCl$_3$ was assumed to attack saturated hydrocarbons, ketones at a tertiary carbon–hydrogen bond, and hydrocarbons at an allylic hydrogen, leading to easier photodegradations. FeCl$_3$ was also effective for the photodegradation of *t*-BuO$_2$H using λ > 300 nm, so that FeCl$_3$ is believed to contribute also to the photodegradation of PP under the same irradiation conditions. The catalytic effect of FeCl$_3$ in photodegradation seems to originate in a redox reaction.

INTRODUCTION

Ferric chloride (FeCl$_3$) has been known as an effective photosensitizer for the photopolymerization of vinyl monomer,[1-3] the photo-induced graft polymerization,[4-6] and the photodegradation of polymer.[7-9]

In our previous article[10] it was reported that FeCl$_3$ markedly accelerates the formation of peroxy radical by catalytic function in a redox manner on the photodegradation of polypropylene (PP) with UV light of λ > 300 nm; in contrast, it depressed the formation of alkyl radical in the system using UV light of λ < 300 nm.

In this study, several model compounds for PP, including irregular structures, were employed in order to clarify the catalytic function of FeCl$_3$ on the photodegradation of PP. The reactions were investigated using electron spin resonance (ESR) spectrometry.
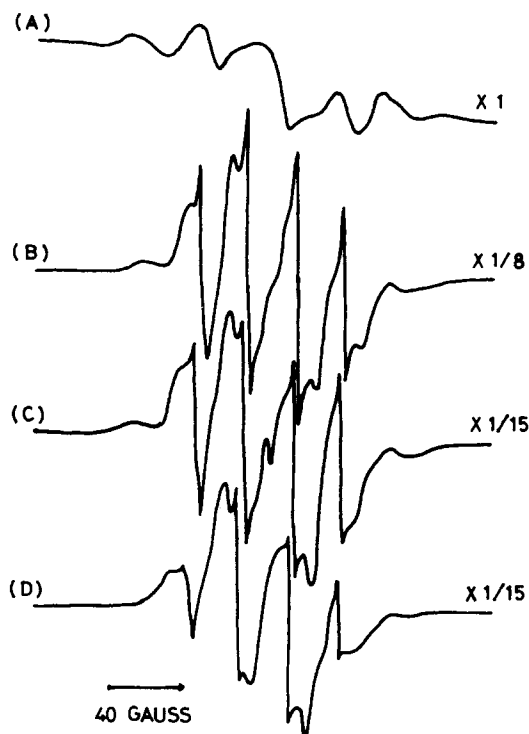
Fig. 1. ESR spectra: (A) n-pentane with added FeCl₃; (B) 2-methylpentane; (C) 2-methylpentane with added FeCl₃; (D) 2,4-dimethylpentane added FeCl₃. Light, high-pressure mercury lamp ($\lambda > 200$ nm); time, 60 min; temperature, 77 K; FeCl₃ added, 0.3 mmol/mol; atmosphere, nitrogen.

EXPERIMENTAL

Sample

Commercial pure-grade reagents, n-pentane (n-P), 2-methylpentane (2-MP), 2,4-dimethylpentane (2,4-DMP), 2-methyl-4-pentanone (2-M4P), and 2,6-dimethyl-4-heptanone (2,6-DM4H), were purified after repeated distillation through a column filled with active alumina. Commercial pure-grade 2-methyl-1-pentene (2-M1P) was purified by distillation. These samples were confirmed to be pure by gas–liquid chromatography. Commercial reagent-grade *tert*-butyl hydroperoxide (t-BuO₂H) and pure-grade anhydrous ferric chloride (FeCl₃) were used without further purification.

Irradiation of UV Light

The samples in a quartz tube for ESR spectrometer were degassed by the freeze–pump–thaw technique in nitrogen atmosphere until no bubbles were observed (8–10 times). The tubes containing 0.10 ml of degassed or undegassed samples were inserted into a quartz Dewar flask for ESR spectrometry and were irradiated with UV light. Irradiation was carried out at 77 K with a high-pressure mercury lamp (Toshiba H 400-P, $\lambda > 220$ nm) and a superhigh-pressure mercury lamp (Ushio Electric Co., 250-D, $\lambda > 220$ nm). In the irradiation with
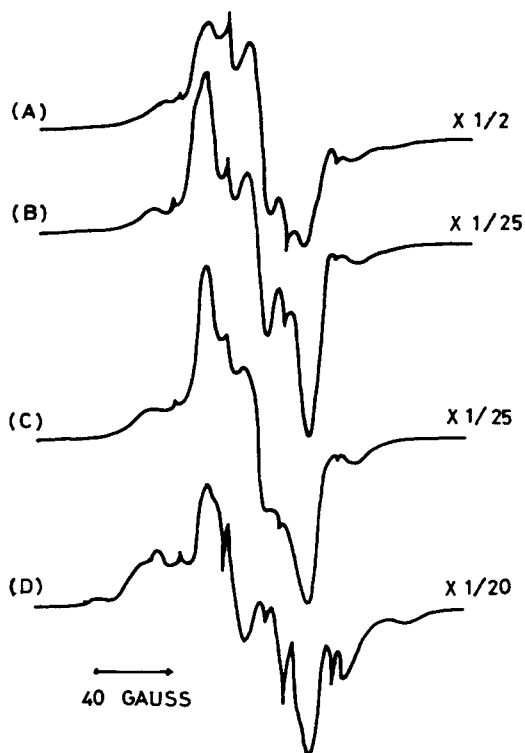
Fig. 2. ESR spectra: (A) 2-methyl-4-pentanone; (B) 2-methyl-4-pentanone added FeCl₃; (C) 2,6-dimethyl-4-heptanone with added FeCl₃; (D) 2-methyl-1-pentene with added FeCl₃. Light, high-pressure mercury lamp ($\lambda > 220$ mn); time, 60 min; temperature, 77 K; FeCl₃ added, 3.0 mmol/mol; atmosphere, nitrogen.

the superhigh-pressure mercury lamp, some modification of wavelength was made using a color filter (Toshiba glass filter).

ESR Measurement

The ESR spectra of the irradiated samples were recorded with a Japan Electron Optics Laboratory JES-ME-X with X band and 100 kHz field modulation.

RESULTS

Photodegradation under Nitrogen—Effect of Ferric Chloride

Typical ESR spectra for irradiated saturated hydrocarbon, ketone, and unsaturated hydrocarbon samples are shown in Figures 1 and 2, respectively.

The n-pentane sample gave a quintet spectrum (splitting constant, 29 gauss). Since only a weak signal was observed, it was believed to be a part of septet spectrum corresponding to a radical, —CH₂—ĊH—CH₃.[11] Irradiated 2-MP and 2,4-DMP samples gave a complex spectrum consisting of a sharp quartet, a broad quartet, and singlet components. Such a spectrum seems to be char-
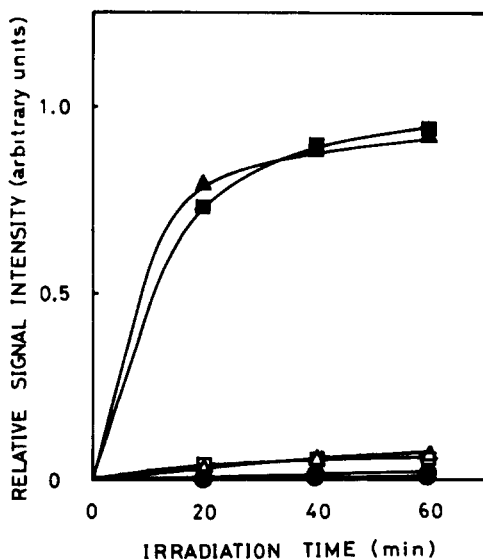
Fig. 3. Effect of FeCl$_3$ on ESR signal intensity: (O) n-pentane; (●) FeCl$_3$ containing n-pentane; (□) 2-methylpentane; (■) FeCl$_3$ containing 2-methylpentane; (△) 2,4-dimethylpentane; (▲) FeCl$_3$ containing 2,4-dimethylpentane.

acteristic of radicals ·CH$_3$,[11,12] ·CH$_2$—CH(CH$_3$)—,[13,14] and CH$_2$=CH—ĊH—,[15,16] respectively.

These hydrocarbons have practically no absorption in the range below 200 nm. As the UV-irradiated quartz tube was observed to indicate a feeble ESR signal, the active species on the tube can be one means of initiation of photodegradation.

Spectra for 2-MP and 2,6-DM4H samples were complex and were analyzed as mixtures of a sharp quartet, a broad quartet, and a singlet. The singlet spectrum seems to belong to an acyl radical, ·CO—CH$_2$—.[17] Irradiated 2-M1P showed a spectrum including a sextet and a sharp quartet. The radical species attributed to the spectra are listed in Table I.

The spectra of FeCl$_3$-containing samples (0.3 mmol FeCl$_3$ per mole saturated hydrocarbon; 3.0 mmol FeCl$_3$ per mole unsaturated hydrocarbon or ketone) bore a close resemblance to those of FeCl$_3$-free samples, but with a marked difference in the signal intensity. The relative signal intensities of the FeCl$_3$-containing samples are shown in Figures 3 and 4. Signal intensities of irradiated samples 2-MP, 2,4-DMP, 2-M4P, 2,6-DM4H, and 2-M1P were greatly increased by the addition of FeCl$_3$, while there was little effect of FeCl$_3$ for n-P and 2-octanone samples.

These facts seem to suggest that FeCl$_3$ accelerates the photodegradation of saturated hydrocarbon and ketone samples containing a tertiary carbon–hydrogen bond or of hydrocarbons having an allylic hydrogen.

Photodegradation under Air—Effect of Ferric Chloride

Undegassed samples were irradiated in air atmosphere at 77 K, and the ESR spectra were recorded at the same temperature. They are shown in Figure 5.

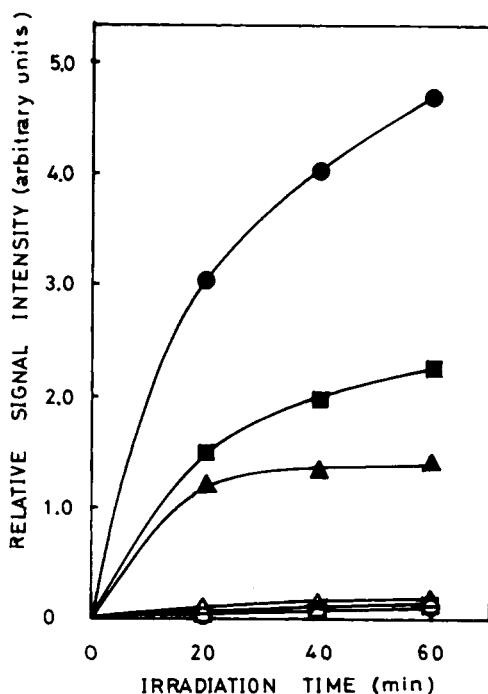Irradiated n-P and 2-MP gave a complex spectrum including a strong asym-

Fig. 4. Effect of FeCl₃ on ESR signal intensity: (O) 2-methyl-4-pentanone; (●) FeCl₃ containing 2-methyl-4-pentanone; (□) 2,6-dimethyl-4-heptanone; (■) FeCl₃ containing 2,6-dimethyl-4-heptanone; (△) 2-methyl-1-pentene; (▲) FeCl₃ containing 2-methyl-1-pentene.

TABLE I

Assignment of Radical Species of Hydrocarbon and Ketone Samples Irradiated at 77 K Under Nitrogen

	Spectra		
Sample	Shape	SCᵃ	Radical species
n-Pentane	broad quintet	29	$—CH_2—\dot{C}H—CH_3$
2-Methylpentane	sharp quartet	23	$\cdot CH_3$
	broad quartet	24	$\cdot CH_2—CH(CH_3)—$
2,4-Dimethylpentane	broad sextet	21	$CH_2=CH—\dot{C}H—CH_2—$
2-Methyl-4-pentanone	sharp quartet	23	$\cdot CH_3$
2,4-Dimethyl-4-heptanone	broad quartet	24	$\cdot CH_2—CH(CH_3)—$
	singlet	10ᵇ	$\cdot CO—CH_2—$
2-Methyl-1-pentene	sharp quartet	23	$\cdot CH_3$
	broad sextet	21	$CH_2=C(CH_3)—\dot{C}H—CH_2—$

ᵃ SC = Splitting constant, gauss.

ᵇ Linewidth at maximum slope, gauss.

metric component at the center of the spectrum, but this component for 2,4-DMP was very weak.   The result of irradiation under air was different from that under nitrogen, in terms of the formation of asymmetric spectrum.   The asymmetric spectrum is attributed to a peroxy radical, ROO·.[18–20]

No differences in the signal shape were observed between irradiated samples under air and nitrogen for ketone and unsaturated hydrocarbon.   However, the relative signal intensities given under air were generally larger than those under nitrogen.
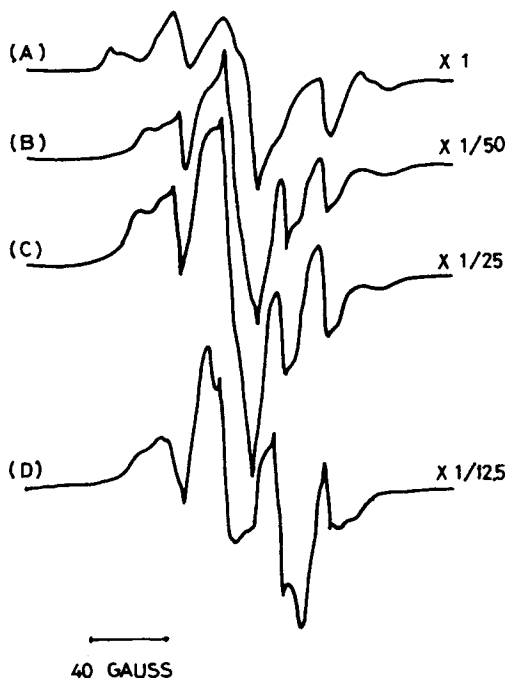
Fig. 5. ESR spectra: (A) n-pentane with added $FeCl_3$; (B) 2-methylpentane; (C) 2-methylpentane added $FeCl_3$; (D) 2,4-dimethylpentane with added $FeCl_3$ irradiated under air. Light, high-pressure mercury lamp ($\lambda > 220$ nm); time, 60 min; temperature, 77 K; $FeCl_3$ added, 3.0 mmol/mol.

On the other hand, $FeCl_3$-containing samples gave somewhat different results, as shown in Figures 6 and 7. The intensities for 2,4-DMP, 2-M4P, 2,6-DM4H, and 2-M1P samples in air increased upon addition of $FeCl_3$. However, the effect of $FeCl_3$ addition was somewhat smaller for air systems than that for nitrogen systems. It seems therefore that there is a specificity of the effect of $FeCl_3$ according to the atmosphere under which the irradiation is carried out.

It was also observed that the relative signal intensities of $FeCl_3$-containing n-P sample were small and that the rate of radical formation was low for 2-MP sample. The depression of photodegradation owing to $FeCl_3$ under air can be explained by assuming the formation of a stable complex between $FeCl_3$ and oxygen.

Wavelength Dependence

The 2-MP, t-BuO_2H (3.0 wt % in 2-MP), and $FeCl_3$-containing samples (concentration of $FeCl_3$, 0.3 mmol/mol) degassed by the freeze–thaw treatment, were irradiated through glass filters, and the specificity of the effect of $FeCl_3$ owing to wavelength was examined.

First, the sample was irradiated with a longer wavelength for 10 min at 77 K under nitrogen, and the ESR spectrum was recorded immediately at 77 K. The sample was subsequently irradiated with a shorter wavelength, and the ESR spectrum was again recorded. Figure 8 shows the effect of wavelength. The 2-MP sample irradiated with $\lambda > 260$ nm gave no ESR signal; however, an ESR spectrum was afforded with $\lambda > 220$ nm, which consisted mainly of a broad quartet.
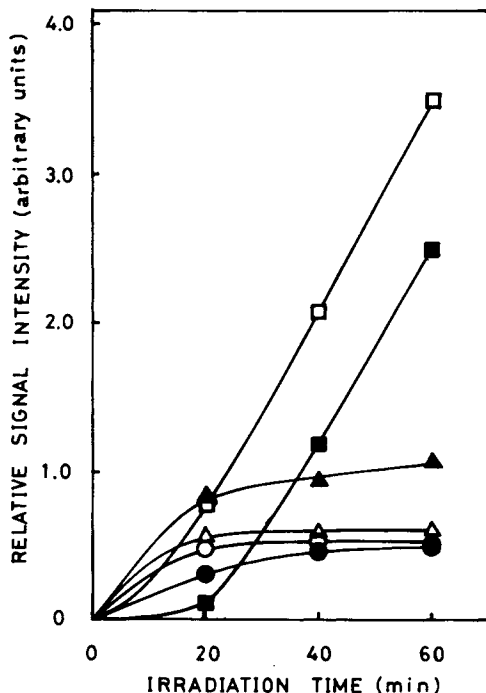
Fig. 6. Effect of FeCl₃ on ESR signal intensity irradiated under air: (O) n-pentane; (●) FeCl₃ containing n-pentane; (□) 2-methylpentane; (■) FeCl₃ containing 2-methylpentane; (△) 2,4-dimethylpentane; (▲) FeCl₃ containing 2,4-dimethylpentane.

The 2,4-DMP sample gave almost the same result. It was inferred that the quartet was attributable to an alkyl radical, $\cdot CH_2-CH(CH_3)-$. FeCl₃-containing 2-MP gave a weak ESR signal with $\lambda > 300$ nm, which became considerably larger by using $\lambda > 220$ nm. With $\lambda > 220$ nm, the intensity of the broad quartet of 2-MP also increased about 2.5 times when FeCl₃ was present. Almost the same effect was observed for the 2,4-DMP sample. Thus, FeCl₃ seems to contribute to the formation of an alkyl radical, $\cdot CH_2-CH(CH_3)-$.

As shown in Figure 9, FeCl₃-containing t-BuO₂H in 2-MP gave a signal with an enhanced asymmetric spectrum ($g_\perp = 2.004$) using $\lambda > 300$ nm. The asymmetric spectrum was assigned to a peroxy radical, $ROO\cdot$.[18–20] The intensity of the spectrum was significantly larger for the FeCl₃-free sample (dotted line). The same effect of FeCl₃ was observed for t-BuO₂H in n-P and 2,4-DMP solvents.

As mentioned above, it is clear that FeCl₃ accelerates markedly the formation of alkyl radical on hydrocarbon containing a tertiary carbon–hydrogen bond, by the irradiation using $\lambda < 300$ nm, and it is also effective for the formation of a $ROO\cdot$ radical in the case of $\lambda > 300$ nm.

DISCUSSION

As FeCl₃ accelerates the formation of radicals from 2-MP, 2,4-DMP, and 2-M1P and not from n-P, under either air or nitrogen, FeCl₃ is believed to promote the photodegradation of hydrocarbons containing a hydrogen atom on a
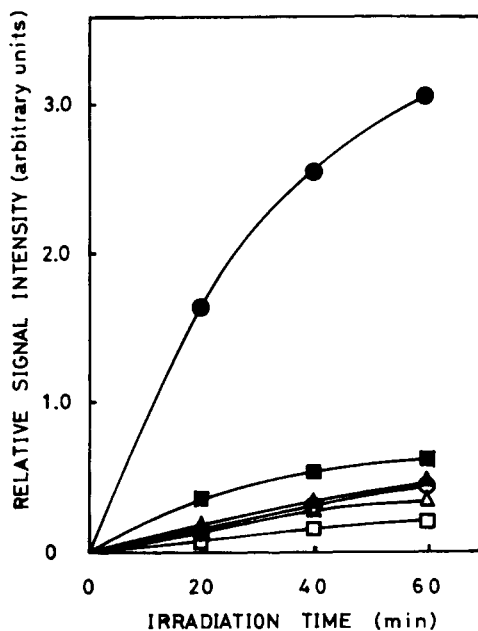
Fig. 7. Effect of $FeCl_3$ on ESR signal intensity irradiated under air: (○) 2-methyl-4-pentanone; (●) $FeCl_3$ containing 2-methyl-4-pentanone; (□) 2,6-dimethyl-4-heptanone; (■) $FeCl_3$ containing 2,6-dimethyl-4-heptanone; (△) 2-methyl-1-pentene; (▲) $FeCl_3$ containing 2-methyl-1-pentene.

tertiary carbon or on an allylic position. These reactions could be explained by the following redox catalytic mechanisms:
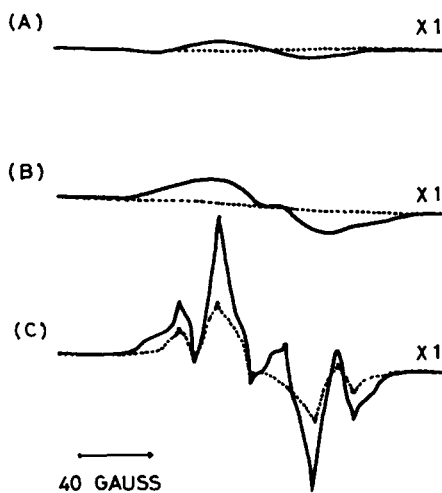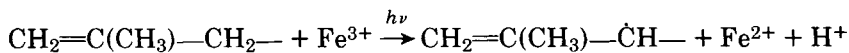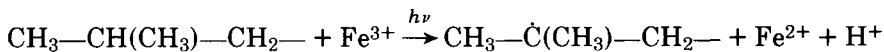
$$CH_3{-}CH(CH_3){-}CH_2{-} + Fe^{3+} \xrightarrow{h\nu} CH_3{-}\dot{C}(CH_3){-}CH_2{-} + Fe^{2+} + H^+$$

$$CH_2{=}C(CH_3){-}CH_2{-} + Fe^{3+} \xrightarrow{h\nu} CH_2{=}C(CH_3){-}\dot{C}H{-} + Fe^{2+} + H^+$$

Fig. 8. Wavelength dependence of ESR spectra: (- - -) 2-methylpentane; (——) $FeCl_3$ containing 2-methylpentane. Light, superhigh-pressure mercury lamp; temperature, 77 K; irradiation time, 10 min; atmosphere, nitrogen. (A) Pyrex glass filter ($\lambda > 300$ nm); (B) UV-29 filter ($\lambda > 260$ nm); (C) no filter ($\lambda > 220$ nm).
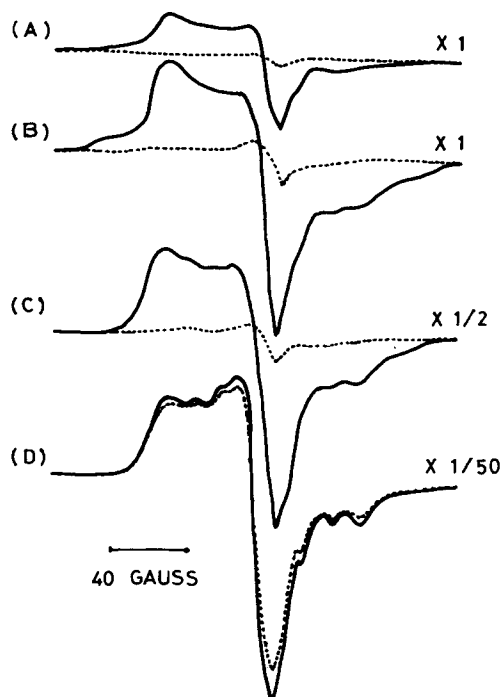
Fig. 9. Wavelength dependence of ESR spectra: (- - -) *tert*-butyl hydroperoxide; (——) FeCl$_3$ containing *tert*-butyl hydroperoxide in 2-methylpentane. (A) VY-42 filter ($\lambda > 370$ nm); (B) UV-35 filter ($\lambda > 335$ nm), (C) Pyrex glass filter ($\lambda > 300$ nm); (D) no filter ($\lambda > 220$ nm).

For ketone samples, the enhanced signal intensities owing to FeCl$_3$ may be caused by the easier formation of the acyl radical ·CO—CH$_2$— and the alkyl radical ·CH$_2$—CH(CH$_3$)—. In that case, it is conceivable that FeCl$_3$ acts more effectively in the formation of alkyl radicals than in the formation of acyl radicals. On the other hand, the photodegradation of 2-octanone, which contains no tertiary carbon–hydrogen bonds, was not affected by FeCl$_3$.

These results seem to suggest that FeCl$_3$ acts on a tertiary carbon–hydrogen bond to promote the cleavage of the bond and to promote the Norrish type-1 reaction forming an acyl radical for the compound containing a carbonyl group. This can be considered as a phenomenon of close interaction between the carbonyl group and FeCl$_3$, which makes the photoenergy very effective.

FeCl$_3$ was also found to act effectively on the photodegradation of t-BuO$_2$H. This can be explained by the following reactions[7]:

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

$$\cdot OH + (CH_3)_3COOH \xrightarrow{h\nu} (CH_3)_3COO\cdot + H_2O$$
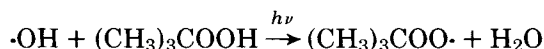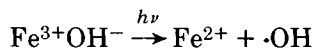
In our previous article it was observed that the photodegradation of PP decreased gradually as the concentration of FeCl$_3$ increased, so that the effect of FeCl$_3$ was believed to be a self-filtration effect of light in the irradiation system. From the experimental results for model compounds in this study, however, FeCl$_3$ was found to have an accelerating effect for the photodegradation essentially of model compounds for PP, which should be true for all PP samples.

References

1. J. H. Baxendale, M. G. Evans, and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946).
2. M. G. Evans, M. Santappa, and N. Uri, *J. Polym. Sci.*, **7**, 243 (1951).
3. F. S. Dainton and R. G. Jones, *Trans. Faraday Soc.*, **63**, 1512 (1967).
4. Y. Ogiwara and H. Kubota, *J. Polym. Sci. Part A-1*, **9**, 2549 (1971).
5. H. Kubota and Y. Ogiwara, *J. Appl. Polym. Sci.*, **16**, 337 (1972).
6. Y. Ogiwara, H. Kubota, and T. Yasunaga, *J. Appl. Polym. Sci.*, **19**, 887 (1975).
7. A. T. Betts and N. Uri, *Chem. Ind.*, **25**, 512 (1967).
8. G. B. Parriskii, E. Ya. Davydov, N. I. Zaitseva, and D. Ya. Toptygin, *Izv. Akad. Nauk SSSR Ser. Khim.*, **2**, 281 (1972).
9. Y. Ogiwara, Y. Kimura, Z. Osawa, and H. Kubota, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 1667 (1977).
10. A. Negishi, Y. Ogiwara, and Z. Osawa, *J. Appl. Polym. Sci.*, **22**, 2953 (1978).
11. B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958).
12. R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
13. M. Iwasaki and K. Toriyama, *J. Chem. Phys.*, **46**, 2852.
14. M. Iwasaki, T. Ichikawa, and K. Toriyama, *J. Polym. Sci. Part B*, **5**, 423 (1967).
15. K. Hamanoue, M. Shimazu, H. Higaki, I. Block, and J. Silverman, *J. Polym. Sci. Part A-2*, **12**, 1189 (1974).
16. L. P. Poole and R. S. Anderson, *J. Chem. Phys.*, **31**, 346 (1959).
17. S. Noda, K. Fueki, and Z. Kuri, *J. Chem. Phys.*, **49**, 3287 (1963).
18. K. U. Ingold and J. R. Morton, *J. Am. Chem. Soc.*, **86**, 3400 (1964).
19. J. C. W. Chien and C. R. Boss, *J. Am. Chem. Soc.*, **89**, 571 (1967).
20. H. Fischer, K. H. Hellwage, and P. Neudörfl, *J. Polym. Sci. Part A*, **1**, 2109 (1963).