

The Effect of Transition Metal Stearates on the Photodegradation of Polyethylene

ZENJIRO OSAWA, NORIO KURISU, KOSAKU NAGASHIMA, and KOSAKU NAKANO, *Department of Polymer Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma, Japan 376*

Synopsis

The effect of a series of transition metal (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) stearates on the photodegradation of a high-density polyethylene was examined mainly by changes in the carbonyl IR absorption of the sample films. Electron spin resonance (ESR) and luminescence spectra of the samples containing the copper stearate were measured. The photochemical reaction of the copper stearate was examined by IR and UV-visible spectroscopies. The iron stearate was the most effective at an early stage of the photodegradation of the polymer, and vanadium and manganese stearates accelerated it, while the copper stearate retarded it. The other metal stearates showed no applicable effect on the photodegradation. The relative intensity of the ESR spectra of the photoirradiated samples and that of the emission spectra of the unirradiated samples at ca. 350 nm decreased with increasing concentration of the copper stearate. An absorption peak at 1580 cm^{-1} decayed, and a new peak at 1740 cm^{-1} appeared with photoirradiation of the copper stearate. Absorption peaks of the copper stearate at 252 and 665 nm decayed also rapidly with photoirradiation of the copper stearate in THF solution. The results suggest that one of the main retardative functions of the copper stearate in the photodegradation of polyethylene was an ultraviolet absorber.

INTRODUCTION

There are many routes that polymers encounter with metals or metallic compounds. For examples, catalyst residues,¹⁻⁵ pigments,^{6,7} metal particles contaminated during machine processing,⁸ insulated wire,⁹⁻¹¹ and so on can be considered. It is also well known that a minor amount of metals or metallic compounds as well as oxygenated groups in substrates play extremely important roles either in the photodegradation or in the thermal degradation of polymers.

No appreciable difference in the catalytic effect of the metallic compounds was observed between photodegradation and thermal degradation of polymeric materials.⁶ However, in our preliminary experiment we found that oxygenated groups produced during the pressing of sample films often suppressed the catalytic effect of the metallic compounds, and metals effective for the thermal degradation behaved as if effective for the photodegradation of polymers. We already reported that if a sample was carefully prepared and free from the oxygenated groups, the effect of some metallic compounds on the photodegradation of the polymers was the reverse of that on the thermal degradation.^{12,13} In this investigation we set out to study the effect of a series of transition metal stearates on the photodegradation of polyethylene. We found that the copper stearate, which was one of the most effective catalysts for the thermal degradation of polypropylene,¹⁴ behaved as a retarder for the photodegradation of polyethylene. We discuss mainly the role of the copper stearates in the photodegradation of

the polyethylene on the basis of IR, ESR, and luminescence spectral data and the photochemical reaction of the copper stearate.

EXPERIMENTAL

Sample. The high-density polyethylene used for all the photodegradation tests was a neat powder, finer than 100 mesh, with the following properties: melt index, 0.7; intrinsic viscosity (molecular weight), 1.6 (6.65×10^4) determined in decalin containing a minor amount of antioxidant (Topanol, kindly presented by ICI, Ltd., Japan) at 135°C; additive, without any stabilizers except metal stearates.

Reagents. Each metal (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) stearate was prepared according to the literature by double decomposition of sodium stearate with corresponding metal salts.¹⁴

Preparation of Sample Films. In glassware (ca. 5 cm³) with a plastic cap, 100 parts of the polymer was shaken and mixed with 0.01, 0.5, and 1.0 part of the transition metal stearates (quantity abbreviated as phr) and glass beads (diam. ca. 3 mm). A weighed amount of the sample was pressed between Teflon sheets with a vacuum press, Shibayama Co. Ltd., SS-VP-50 type, under reduced pressure (10^{-2} Torr, 150 kg/cm²) at ca. 130–140°C to give 0.07–0.08 mm thick, 40 mm diameter films. Prior to photoirradiation the films were examined and found to be infrared-spectrally free from oxygenated groups.

Photoirradiation. Photoirradiation of the sample was carried out with a Riko Rotary Photochemical Apparatus, RH 400-10 W, a merry-go-round type. Each film was placed in quartz glassware 5 cm distant from the light source, a Riko high-pressure mercury lamp (main wavelengths 2537, 2900, and 3650 Å) and irradiated with and without a glass tube filter ($\lambda > 3000$ Å). The glasswares, rotating on their axis, rotated around the mercury lamp and were immersed in a running water bath. Photoirradiation of the copper stearate in bulk and/or in THF solution (in a quartz cell) was carried out with a Toshiba high-pressure mercury lamp at ambient temperature.

Infrared Spectra

Infrared spectra of each film sample were recorded on a Hitachi 124 double-beam grating spectrometer. The changes in IR spectra at 1720 cm⁻¹ due to carbonyl groups were analyzed by a baseline method, and the effect of the metal stearates was estimated. In the case of the copper stearate, measurement was made by a KBr pellet method.

Ultraviolet-Visible Spectra

Ultraviolet-visible spectra were obtained using a Hitachi double-beam Model 124 spectrometer.

Emission Spectra

Emission spectra were recorded using a Hitachi MPF-2A fluorescence spectrophotometer with a xenon source and a photomultiplier.

ESR Spectra

ESR spectra were recorded with an X-band spectrometer with 100 kc field modulation (Japan Electron Optics Laboratory Co., Model JES-ME-X) at 77 K immediately after photoirradiation at 77 K in vacuo for 1 hr. For the ESR measurement, powdery samples containing 0.5, 2.5, and 5.0 phr of the copper stearate were used.

RESULTS AND DISCUSSION

Effect of Transition Metal Stearates

The relative effects of the transition metal stearates on the photodegradation of the polyethylene were compared by the simultaneous irradiation of the metal-containing films and neat film with light from a high-pressure mercury lamp without a filter. As shown in Figure 1, the infrared spectrum of a typical neat film changes remarkably in the regions of ca. 1720 cm^{-1} due to carbonyl groups, $3300\text{--}3400\text{ cm}^{-1}$ due to hydroxyl groups, ca. 1303 cm^{-1} due to an amorphous region, ca. 909 cm^{-1} due to unsaturated groups.^{15,16} Typical examples shown in Figure 2 indicate that the extent of the changes in these regions of the infrared spectra are apparently affected by the metal stearates added to the sample films.

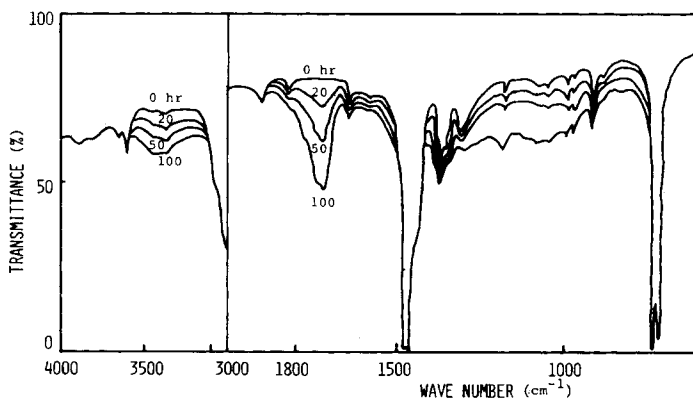


Fig. 1. Changes in IR spectrum of PE during photoirradiation.

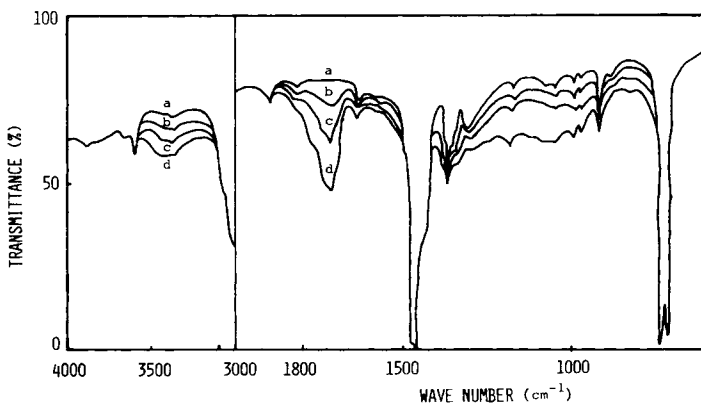


Fig. 2. Changes in IR spectrum of PE film during photoirradiation: (a) PE (0 hr); (b) PE + Cu (0.5 phr) (50 hr); (c) PE (50 hr); (d) PE + V (0.5 phr) (50 hr).

In order to clarify the effect of each metal stearate on the photodegradation of the polymer, plots of the relative optical density at 1720 cm^{-1} of the samples against irradiation times are shown in Figure 3. The figure shows that the content of carbonyl groups increases during the photoirradiation and that some of the transition metal stearates affect appreciably the photodegradation of the polyethylene at 0.5 phr concentration. Iron stearate is the most effective at an early stage of the photodegradation of the polymer, and vanadium and manganese stearates accelerate it, while copper stearate retards it. Other stearates show no appreciable effect on the photodegradation.

The results obtained in this photodegradation of the polyethylene are quite different from those obtained previously in the thermal degradation of polypropylene.¹⁶ For examples, cobalt, chromium, and copper stearates accelerated the thermal degradation of the polypropylene, but these metal stearates were not effective catalysts for the photodegradation of polyethylene, and copper stearate even acted as retarder. In our preliminary experiment, we observed that most of the transition metal stearates accelerated the photodegradation of the polyethylene. And the more effective the metal was in the thermal degradation of the polypropylene, the more effective it was in the photodegradation of the polyethylene. However, the present work apparently suggested that a minor amount of the oxygenated groups such as carbonyls formed during the pressing films concealed the effect of the metal stearate in the preliminary experiment.

Finding that vanadium stearate was effective for the photodegradation of polyethylene and copper stearate retarded it, the concentration dependence of the both metal stearates was examined. Plots of the optical density of the samples containing the vanadium and the copper stearate at 1720 cm^{-1} against irradiation times are shown in Figures 4 and 5, respectively. Figure 4 shows that

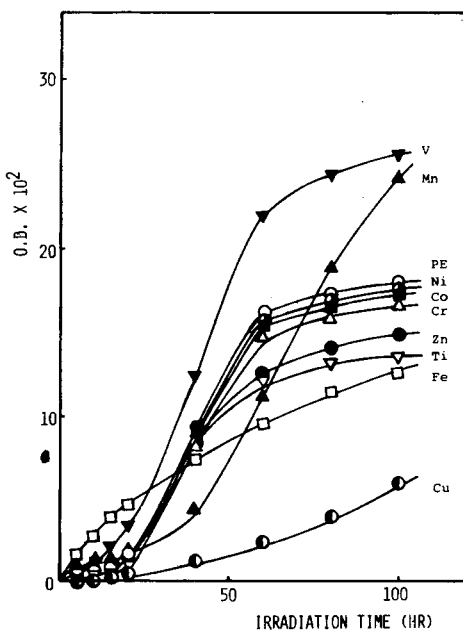


Fig. 3. Changes in carbonyl absorption (at 1720 cm^{-1}), without a filter.

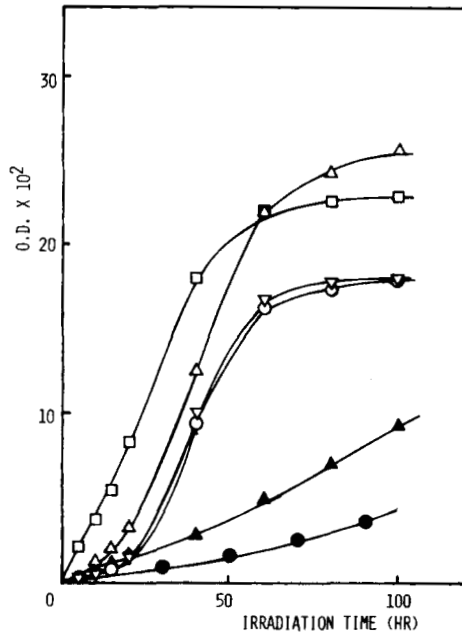


Fig. 4. Changes in carbonyl absorption of PE films containing vanadium stearate (at 1720 cm^{-1}). Without a filter: (○) 0 phr; (▽) 0.01 phr; (△) 0.5 phr; (□) 1.0 phr. With a filter: (●) 0 phr; (▲) 0.5 phr.

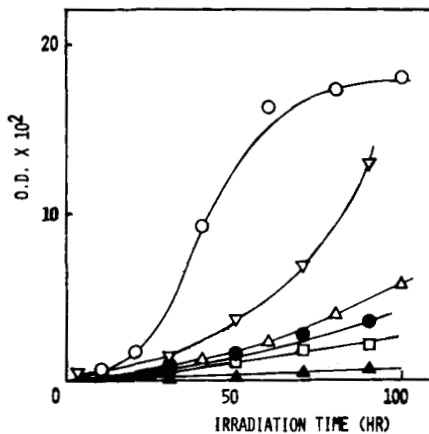


Fig. 5. Changes in carbonyl IR absorption of PE films containing copper stearate (at 1720 cm^{-1}). Without a filter: (○) 0 phr; (▽) 0.01 phr; (△) 0.5 phr; (□) 1.0 phr. With a filter: (●) 0 phr; (▲) 0.5 phr.

the accelerative effect of the vanadium stearate on the photodegradation of the polymer increases with increasing concentration of the vanadium stearate. In addition, the increase in carbonyl content of the films irradiated through a glass filter was much less than that of the samples irradiated without a glass filter. Figure 5 demonstrates that the retardation effect of copper stearate on the photodegradation of the polymer is enhanced by increase in the concentration of the copper stearate.

Inhibitive Effect of Copper Stearate

ESR Spectra. Since the radical mechanism of the photodegradation of polymers is well known and an ESR method has been widely used to measure the relative concentration of radicals produced during the photodegradation, ESR spectra of the polyethylene containing the copper stearate were measured at 77 K immediately after the irradiation in vacuo at 77 K for 1 hr and are shown in Figure 6. It was already reported that the photoirradiation of polyethylene yielded an eight-line spectrum with 21 gauss, which was assigned to a single radical of type $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_3$ produced by the Norrish-type I reaction at carbonyl groups contained in a minor amount in the polymer.¹⁵ The ESR spectra obtained are similar to those of the literatures,¹⁵ and the relative intensity of the signal decreases with increasing concentration of the copper stearate. If the concentration of the radicals produced by the photoirradiation is proportional to the degree of the degradation of the polymer, the results obtained in the ESR study are consistent with those of the IR study mentioned above.

Luminescence Spectra. In order to elucidate the retardative action of the copper stearate on the photodegradation of the polyethylene, luminescence spectra of the unirradiated samples were measured (see Fig. 7). The emission spectra observed at ca. 350 nm were assigned to carbonyl groups, mostly aldehyde attached to macromolecular chain by Charlesby and Partridge.¹⁶ The spectra shown in Figure 7 are similar to those obtained in a previous paper.¹³ However, the relative intensity of the spectra at ca. 350 nm decreases with increasing concentration of the copper stearate in the polymer. If the intensity of the emitted light is decreased by the consumption of the photoenergy absorbed by the samples, the enhancement of the photochemical reaction may be inversely proportional to the intensity of the spectra. However, the photodegradation of the polyethylene was retarded by the copper stearate. Therefore, these results suggest the possibility that effective light for the photodegradation of the polymer is mainly consumed by the photochemical reaction of the copper stearate itself.

Photochemical Reaction of Copper Stearate. The photoirradiation of

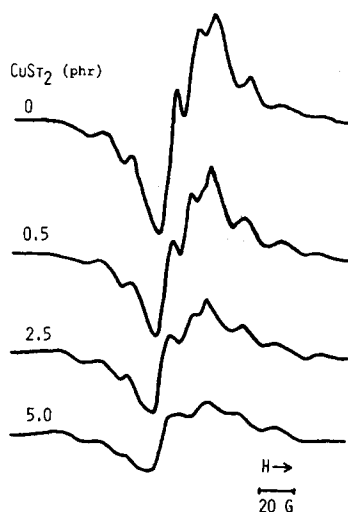


Fig. 6. ESR spectra of PE containing copper stearate irradiated and measured at 77 K.

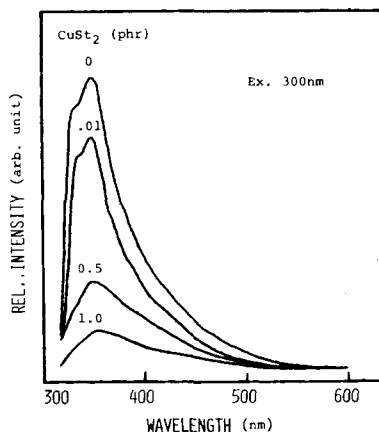


Fig. 7. Emission spectra of PE containing copper stearate.

the copper stearate was carried out in bulk and in THF solution at ambient temperature. IR spectra of copper stearate irradiated in THF solution shown in Figure 8 indicate that the absorption peak at 1580 cm^{-1} due to carboxylate anion¹⁷ of the copper stearate decays and that a new absorption peak at 1740 cm^{-1} appears and gradually increases with the photoirradiation of the copper stearate. The change in these regions was faster than that in IR spectra of the copper stearate in bulk.

In the case of the ultraviolet-visible absorption spectra, copper stearate shows three absorption peaks, namely, at 252 nm due to $\pi-\pi^*$ transition of the carboxylate, at 370 nm due to $n-\pi^*$, and 665 nm due to $d-d^*$ transition of copper(II). As shown in Figure 9, the absorption peaks at 252 and 665 nm decay rapidly with the photoirradiation of copper stearate in THF solution. Although identification of the products is under investigation, the results apparently indicate that the photochemical reaction of the copper stearate does occur readily.

The role of the metallic compounds in the photodegradation of polymers is a very complicated one. The following functions of the metallic compounds are considered: energy sensitizer (or quencher), acceleration of decomposition of hydroperoxide to radicals or to stable products, ultraviolet screening, and so on. Therefore, it is difficult to come to a definite conclusion regarding the retardative

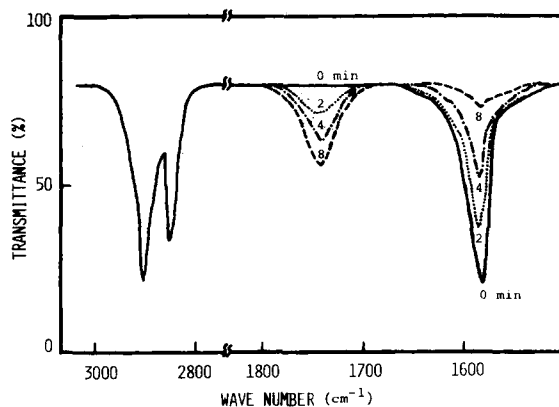


Fig. 8. Changes in IR spectrum of copper stearate during photoirradiation at room temperature.

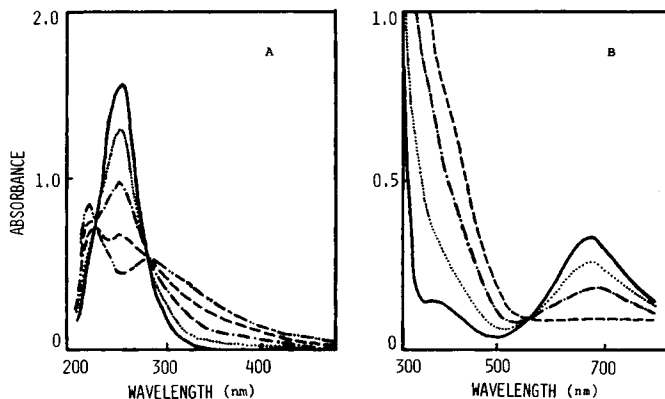


Fig. 9. Changes in UV-visible absorption spectra of copper stearate during irradiation at room temperature. (a) $[CuSt_2]$ $2.1 \times 10^{-4} M$: (—) 0 min; (⋯) 0.5 min; (---) 1.0 min; (- - -) 1.5 min; (- - -) 2.0 min. (b) $[CuSt_2]$ $1.3 \times 10^{-3} M$: (—) 0 min; (⋯) 2 min; (---) 4 min; (- - -) 6 min.

action of copper stearate in the photodegradation of the polyethylene. However, the results mentioned above suggest that one of the main retardative functions of copper stearate in the photodegradation of the polymer is that of ultraviolet absorber.

References

1. S. Fujiwara, *Instrumental Analysis of Polymers*, Hirokawa, Tokyo, 1961, p. 80.
2. R. C. Voter, *Analytical Chemistry of Polymer*, Part 1, *Analysis of Monomer and Polymeric Materials, Plastics-Resins-Rubber-Fibers*, Interscience, New York, 1959, p. 16.
3. R. A. Auduze, *Anal. Chem.*, **29**, 90 (1957).
4. G. P. Fratkina, *Zavodskaya Lab.*, **24**, 1373 (1958); *Z. Anal. Chem.*, **169**, 229 (1959).
5. W. T. Bolleter, *Anal. Chem.*, **31**, 201 (1959).
6. T. Takahashi and K. Suzuki, *Kobunshi Kagaku (Polym. Chem.) Japan*, **21**, 487, 494, 498 (1964); **23**, 792 (1966).
7. P. G. Kelleher, *J. Appl. Polym. Sci.*, **10**, 843 (1966).
8. P. Richeter, *Macromolecules*, **3**, 262 (1972).
9. R. H. Hansen, C. A. Russell, T. De Benedictis, W. M. Martin, and J. V. Pascale, *J. Polym. Sci. A*, **2**, 587 (1964).
10. R. H. Hansen, T. De Benedictis, and W. M. Martin, *Polym. Eng. Sci.*, **5**, 223 (1965); *Trans. Inst. Rubber Ind.*, **39**, 290 (1963).
11. W. L. Hawkins, M. G. Chan, and G. L. Link, *Polym. Eng. Sci.*, **11**, 377 (1971).
12. Z. Osawa, T. Ishizuka, Y. Ogiwara, H. Suzuki, and H. Ishikawa, *J. Appl. Polym. Sci.*, **16**, 955 (1972).
13. Z. Osawa and K. Nakano, *J. Polym. Sci. Symp. No. 55*, 267 (1976).
14. Z. Osawa, T. Shibamiya, and K. Matsuzaki, *Kogyo Kagaku Zasshi*, **71**, 552 (1968).
15. K. Tsuji, *Adv. Polym. Sci.*, **12**, 131 (1973); *Polym. Plast. Technol. Eng.*, **9**(1), 1 (1977).
16. A. Charlesby and R. H. Partridge, *Proc. R. Soc. London Ser. A*, **283**, 312, 329 (1965).
17. R. Matsuura, *Nippon Kagaku Zasshi*, **86**, 560 (1965).

Received August 2, 1977

Revised September 21, 1978