Catalytic Action of Metallic Salts in Autoxidation and Polymerization.   VI.   The Inhibitive Effects of Transition-Metal N,N-Diethyldiselenocarbamates on the Thermal Oxidative Degradation of Isotactic Polypropylene

ZENJIRO OSAWA, TAKASHI ISHIZUKA, and YOSHITAKA OGIWARA, *Department of Polymer Chemistry, Faculty of Engineering, Gunma University; Kiryu City, Gunma, Japan*
and
HIDEO SUZUKI and HISAO ISHIKAWA, *Research Institute of Fujikura Wire and Cable Ltd., Kōtō-ku, Tokyo, Japan*

Synopsis

Transition-metal (Zn, Ni, Pd, Cu, Cr, Co) N,N-diethyldiselenocarbamates were prepared, and the inhibitive effects of these compounds on the thermal oxidative degradation of isotactic polypropylene, both in the presence and absence of copper stearate as oxidation accelerator, were examined by conventional oxygen uptake.   In both cases, all metal selenocarbamates showed a pronounced inhibitive effect on the degradation of the polymer, especially Zn and Ni selenocarbamates.   The inhibitive action of these metal selenocarbamates was discussed from the viewpoint of viscosity change and carbonyl and hydroperoxide contents.

INTRODUCTION

Since isotactic polypropylene was successfully prepared by Natta, it has been adopted as a plastic material in many fields, especially as an insulating material for electric cables.   This popularity is attributed to its low density and the accompanying excellent insulating properties, its high softening point, its low solubility in common solvents, its negligible water absorption, and its mechanical strength.   However, polypropylene is less resistant to oxidative degradation than linear polyethylene, because of a number of labile tertiary hydrogen, atoms in its structure.   The degradation is also markedly accelerated in the presence of metallic compounds, especially copper.   Therefore, inhibition of the degradation of the polymer is extremely important, and a pioneering investigation on the copper-catalyzed thermal oxidative degradation was made by a research group at Bell Telephone Laboratories.[1–3]   Subsequent studies have been made by others.[4–16]

In a previous paper of this series,[16] we reported that diethyldiselenocarbamatocobalt(III) (abbreviated Co(III) Se-carbamate) could inhibit thermal

oxidation of isotactic polypropylene both in the presence and absence of copper stearate.   Thus, we prepared some transition-metal N,N-diethyl-diselenocarbamates, and the inhibitive effects of the thermal degradation of the polymer, both in the presence and absence of copper stearate, were examined.   We found pronounced inhibitive effects in all transition-metal carbamates examined.   Among them, Zn(II) and Ni(II) Se-carbamates were especially excellent.

EXPERIMENTAL

Preparation of Transition-Metal Diethyldiselenocarbamates

Carbon diselenide was prepared according to the procedure of Gattow and Drager[17] using an apparatus shown in Figure 1.   Thus, 50 g of solid selenium was put into a quartz cell (A in Fig. 1), and dichloromethane was introduced by dry nitrogen stream which was previously passed through a reducing column for ca. $^1/_2$ hr to replace air in the cell.   The temperature was then raised to 600°C (at this temperature selenium was in a molten state).   Upon heating, golden-yellow carbon diselenide was produced slowly by the following reaction:

$$CH_2Cl_2 + 2Se \rightarrow CSe_2 + 2HCl$$
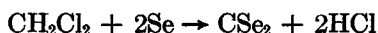
After steam distillation of a mixture of carbon diselenide and unreacted dichloromethane, carbon diselenide was separated from the aqueous layer by a separatory flask.

The preparative method of the ligand was the same as that of the procedure of Furlani et al.[18]   Into a 100-ml round-bottomed flask, cooled to about −10°C and fitted with a stirrer, was poured a sodium hydroxide solution (0.9 g in 40 ml H_2O), and then a flow of nitrogen which was previously passed through a reducing column was admitted for $^1/_2$ hr.   Then a slight excess of diethylamine was added, and finally, very slowly (about 2 hr) and stirring vigorously, a solution of carbon diselenide in purified dioxane (3.15 g in 30 ml) was added.   In order to avoid possible insoluble impurities arising
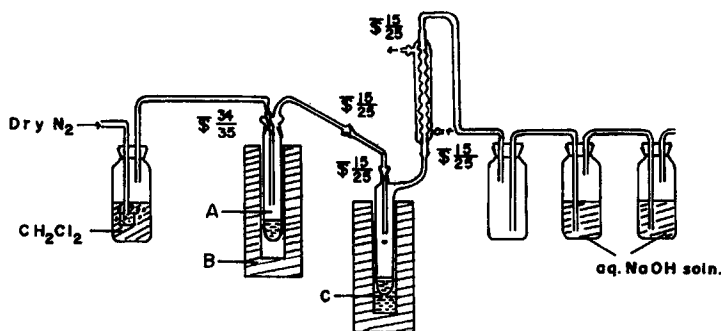

Fig. 1. Apparatus for the preparation of CSe_2: (A) quartz cell; (B) electric furnace; (C) Dry Ice and methanol.

generally from polymerization of carbon diselenide, the solution was filtered and then used for the preparation of complexes.

The resulting solution of sodium diethyldiselenocarbamate was mixed with an aqueous solution of the appropriate metal chlorides in stoichiometric amounts. Upon such treatment, the corresponding complexes precipitated. The precipitants were dissolved with chloroform and reprecipitated into n-hexane through a glass filter. Thus, transition-metal diethyldiselenocarbamates obtained were washed with n-hexane and dried under vacuum. The transition-metal diethyldiselenocarbamates prepared were as follows:

Zn(II) Se-carbamate:pale yellow
Ni(II) Se-carbamate:deep green-brown
Pd(II) Se-carbamate:red-orange
Cu(II) Se-carbamate:red-brown
Cr(III) Se-carbamate:blue-gray
Co(III) Se-carbamate:deep red-brown.

Thermal Oxidative Degradation

The isotactic polypropylene used for all oxidation tests was neat powder, finer than 100 mesh, with the following properties: crystallinity, 60%, determined by infrared spectral analysis; intrinsic viscosity, 1.3, determined in decalin containing a minor amount of antioxidant (Topanol, kindly presented by ICI (Japan) Ltd.) at 135°C; ash, 0.005–0.01%; additive, without any stabilizers. In a mortar, 100 parts of polymer was carefully mixed with 0.25 part of transition-metal diethyldiselenocarbamates prepared, with or without 0.5 part of copper stearate.

The thermal oxidation was carried out using 100-mg samples under atmospheric pressure at 120° and 140°C with a conventional oxygen absorption apparatus prepared in our laboratory. Double determinations were made for each sample and the inhibitive effect of each compound was estimated by the oxygen uptake curves.

Determination of Property Changes

For polymers containing Ni(II) and Zn(II) Se-carbamate and pure polymer, samples with different degrees of oxidation (the amount of absorbed oxygen was 0–40 ml/g polymer) were prepared, and the changes in the following properties were examined.

Intrinsic Viscosity. Intrinsic viscosity was measured in decalin containing a minor amount of antioxidant (Topanol) at 135°C under nitrogen atmosphere.

Carbonyl Group. Carbonyl groups were determined by infrared analysis using a KBr pellet method.

Hydroperoxide. 50-mg samples were added to triangle flasks containing ethanol (20 ml), glacial acetic acid (5 ml), and saturated aqueous solution of potassium iodide (1 ml), and heated at 80°C under nitrogen atmosphere

for 2 hr.   Iodine liberated was determined with $0.01N$ sodium thiosulfate. It was confirmed that no hydroperoxide was formed by this procedure.

RESULTS AND DISCUSSION

In this series of experiments, we have examined the effect of various metallic compounds on the thermal oxidative degradation of polymers. In a previous paper, we examined the effect of some cobaltic compounds on the degradation of isotactic polypropylene, and we found that Co(III) Se-carbamate was an excellent inhibitor for the thermal oxidative degradation of the polymer on the basis of the thermal stability estimated by the oxygen uptake curves.   Furthermore, we proposed that metallic compounds with an ionic bonding character were extremely effective catalysts for the degradation of the polymer, while cobaltic compounds with a highly covalent character did show pronounced inhibitive effect.   Thus, we prepared some transition-metal Se-carbamates, including Co(III) Se-carbamate, and examined the effect of metals in the carbamates on the thermal degradation.

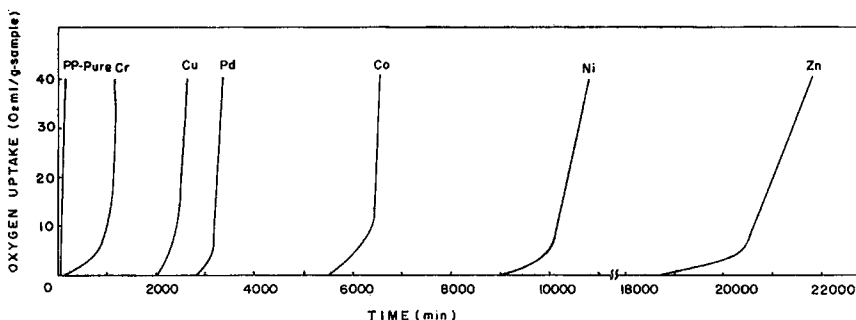Oxygen uptake curves for isotactic polypropylene containing various

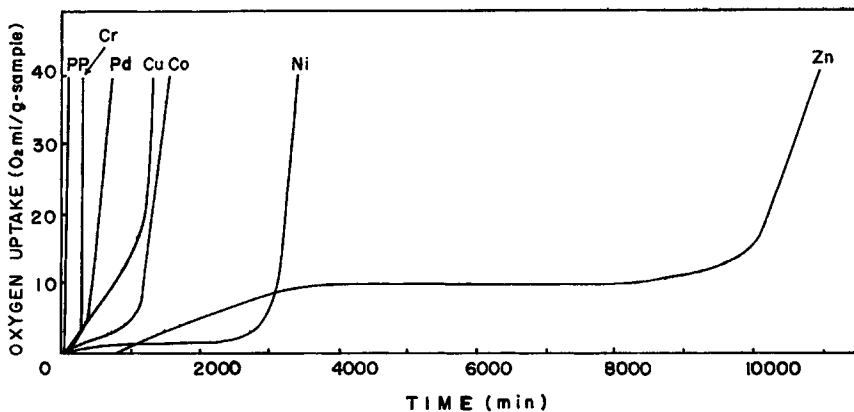Fig. 2. Oxygen uptake curves at 120°C.

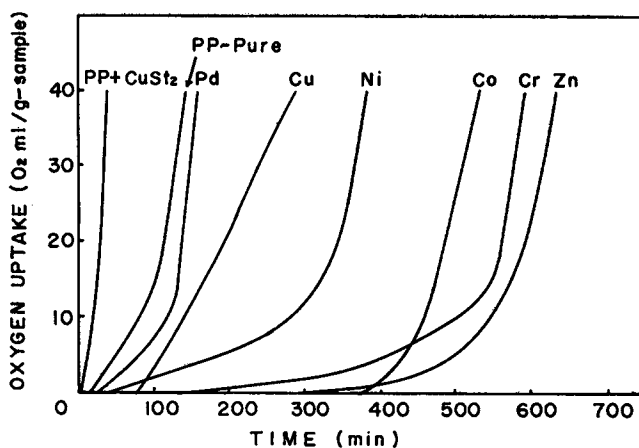Fig. 3. Oxygen uptake curves at 140°C.

Fig. 4. Oxygen uptake curves, of polymer containing metal Se-carbamates with copper stearate at 120°C.

metal Se-carbamates at 120° and 140°C are shown in Figures 2 and 3, respectively. All metal Se-carbamates examined show pronounced inhibitive effect on the thermal oxidative degradation of isotactic polypropylene, particularly at 0.25 pph, but the inhibitive effect is extremely affected by the kind of centered metal.

During an investigation of copper-catalyzed thermal oxidative degradation of polypropylene at the Bell Telephone Laboratories,[1-3] it was observed that in the presence of copper, the autocatalytic period is absent or vestigial and the oxidation reaction rapidly attains a catalytic constant. Because of this catalytic action of copper and copper compounds, industrial application for cables was extremely limited, and extensive studies for the inhibition of the copper-catalyzed thermal oxidative degradation of the polymers have been carried out by many researchers.[4-16] In a previous paper,[16] since we found that Co(III) Se-carbamate could inhibit the copper stearate-catalyzed degradation of polypropylene, the effect of various metal Se-carbamates on the copper stearate-catalyzed degradation of the polymer was examined at 120°C. In Figure 4, the oxygen uptake curves of isotactic polypropylene containing various metal Se-carbamates (0.25 pph) with copper stearate (0.5 pph) are shown. As shown in the figure, metal Se-carbamates also inhibit the copper stearate-catalyzed thermal oxidative degradation of the polymer. However, the inhibitive effect of each metal Se-carbamate is different from that in the absence of copper stearate. This is probably due to the different interaction of metal Se-carbamate and copper stearate.

In order to elucidate the inhibitive action of metal Se-carbamates on the thermal degradation of the polymer, samples with different degrees of oxidation (the amount of absorbed oxygen was 0–40 ml/g polymer) were prepared for Ni(II) and Zn(II) Se-carbamates, and the changes in intrinsic viscosity, carbonyl groups, and hydroperoxide were examined.
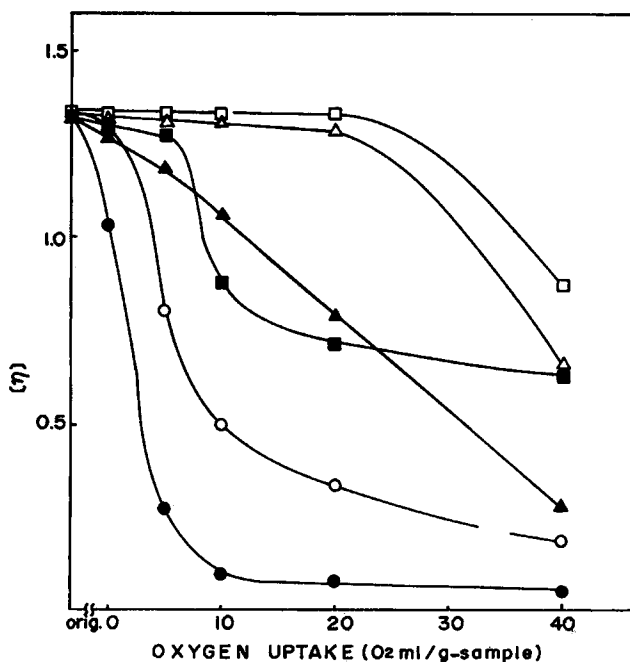
Fig. 5. Intrinsic viscosity vs. cumulative oxygen uptake. O: Pure PP, 120°C; ●: pure PP, 140°C; △: with Ni, 120°C; ▲: with Ni, 140°C; □: with Zn, 120°C; ■: with Zn, 140°C.

The intrinsic viscosities were plotted against cumulative oxygen uptake and are shown in Figure 5. In the case of pure polypropylene, intrinsic viscosity drops sharply during absorption of about 5–10 ml/g polymer, while in the case of polymer containing Ni(II) or Zn(II) Se-carbamate, no appreciable change in intrinsic viscosity occurs at this absorption region. In other words, at the same cumulative oxygen uptake, the intrinsic viscosity of the polymer containing metal Se-carbamates is higher than that of pure polymer. Furthermore, the decrease in intrinsic viscosity is affected by the oxidation temperature, and it is larger at 140°C than at 120°C. Since a decrease in intrinsic viscosity is attributed to chain-scission reaction,[6] it is probable that metal Se-carbamates plays a very important role in chain-scission reactions.

Changes in carbonyl groups during the degradation of the polymer could be determined by infrared spectral analysis, and this method was extensively utilized to estimate the extent of the degradation. Thus, the carbonyl group content during the degradation as measured by an infrared spectral analysis was plotted against cumulative oxygen uptake, and is shown in Figure 6. The carbonyl content also demonstrates the effect of metal Se-carbamate on the thermal oxidation of the polymer. At the same amount of oxygen absorption, the content of carbonyl groups of pure polymer is higher than that of the polymer containing metal Se-carba-
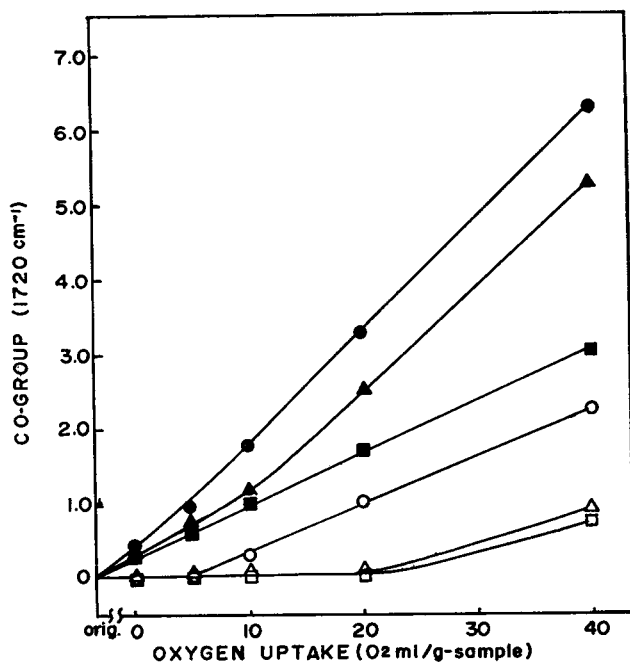
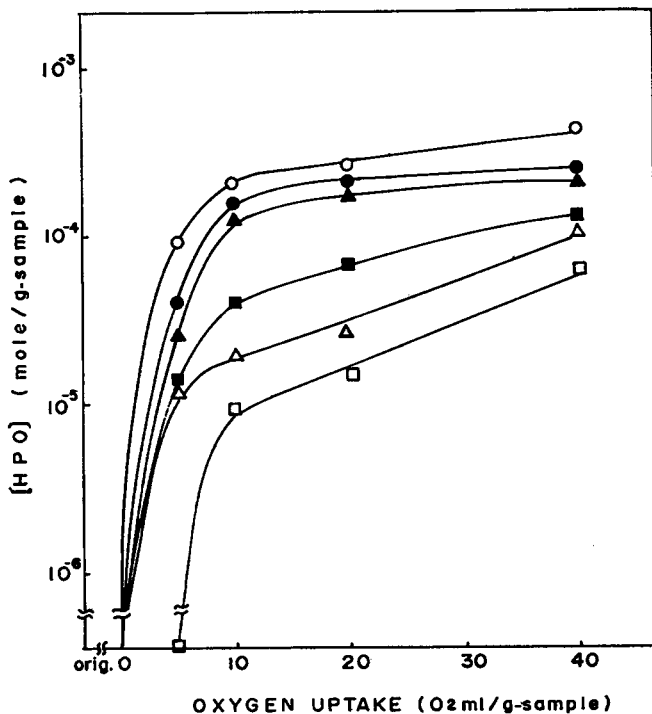Fig. 6. Carbonyl content vs. cumulative oxygen uptake.   Symbols as in Fig. 5.

Fig. 7. Hydroperoxide content vs. oyxgen uptake.   Symbols as in Fig. 5.

mates. This behavior is consistent with the observed decrease in intrinsic viscosity.

Bell and co-workers[20] have ascribed the formation of such products to the decomposition of the radical RO·, which may form during the decomposition of peroxides. Others have also indicated that such radicals are responsible for the formation of various oxidation products.[21-26] Therefore, these results may indicate that metal Se-carbamates decompose unstable reaction intermediates to relatively stable products such as alcohols.

The hydroperoxide content of oxidized polymer was measured by iodometry, and was plotted against cumulative oxygen uptake in Figure 7. The hydroperoxide content of polymer containing metal Se-carbamates is lower than that of pure polymer. The results suggest that metal Se-carbamates accelerate the decomposition of hydroperoxide formed during the oxidation of the polymer to stable products such as alcohols rather than carbonyl compounds. Furthermore, it was reported that metal dialkyldithiocarbamates were effective inhibitors as hydroperoxide decomposers for the oxidation of polyolefins.[7,27-29]

The results mentioned above showed that all transition metal Se-carbamates examined are effective inhibitors of the thermal oxidative degradation of isotactic polypropylene, both in the presence and absence of copper stearate as oxidation accelerator, especially Zn(II) and Ni(II) Se-carbamates. The changes in viscosity, carbonyl groups, and hydroperoxide during the degradation suggest that these metal Se-carbamates act as hydroperoxide decomposers. We shall report on this work in our next publication.

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