# Initiation during Cobalt(III) Catalyzed Oxidation of Polypropylene

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ABSTRACT: The effect of the addition of $\alpha,\alpha$-diphenyl-$\beta$-picrylhydrazyl to the cobalt(III) acetylacetonate catalyzed autoxidation of atactic polypropylene in the solid phase was studied in detail to obtain information about the initiation reaction. The reaction temperature ranged from 110 to 130°, oxygen and polypropylene concentrations varied from 25 to 100%, and the catalyst and inhibitor concentration varied from (6.0 to 60.0) $\times 10^{-8}$ mol and from (1.0 to 15.0) $\times 10^{-8}$ mol, respectively. The reciprocal of the induction time was found to be directly proportional to concentrations of oxygen, substrate, and catalyst. An initiation mechanism that is in agreement with the overall mechanism proposed for the catalyzed oxidation of polyolefins has been put forward to explain the experimental results.

Stivala, Reich, and Kelleher[2] proposed a scheme to satisfactorily explain their kinetic data on the thermal oxidation of isotactic polypropylene. Since then, the authors have used the scheme for the uncatalyzed autoxidation of various polyolefins in the bulk phase, *e.g.*, atactic polypropylene and poly(butene-1).[3-5] This scheme was subsequently modified by the authors to accommodate the metal catalyzed autoxidation of polyolefins.[6-9] In this case, the initiation step was assumed to be kinetically first order with respect to catalyst, substrate, and oxygen concentrations. Recently, Bawn and Chaudhri[10] have also used a similar mechanism in explaining their kinetic results on the metal salt catalyzed autoxidation of polypropylene *in solution*. However, from induction period studies they found that whereas the rate of initiation dependency upon oxygen and substrate concentrations was approximately first order, the dependency on catalyst concentrations (manganese salts) was approximately half order. They attributed the latter to the formation of Mn(II) from Mn(III), with the Mn(II) reacting with peroxy radicals. However, it would appear that other factors could also have entered which could interfere with the precise determination of kinetic orders by Bawn and Chaudhri. Thus, these authors used $\beta$-naphthol in determining induction periods. This inhibitor is known to react with peroxy radicals to form hydroperoxides which could then further react with the metal catalyst, thereby complicating interpretations from their data. Therefore, it behooved us to reexamine the initiation step during the autoxidation of atactic polypropylene *in the bulk phase* in the presence of cobalt(III) acetylacetonate using $\alpha,\alpha$-diphenyl-$\beta$-picrylhydrazyl, which adds to free radicals rapidly without the formation of hydroperoxides.

## Experimental Section

(A) **Starting Materials.** (1) **Atactic Polypropylene.** An uninhibited sample of atactic polypropylene (APP) from Avisun Corp. was purified as described previously.[4] Upon ignition, the APP sample gave an ash content of 0.008%. A number-average molecular weight, obtained by osmometry, was about 30,000.

(2) **Catalyst.** Cobaltic acetylacetonate (2,4-pentanedionate) was obtained from J. T. Baker Chemical Co. (the highest purity grade) and used without further purification, mp 210–213°.

(3) **$\alpha,\alpha$-Diphenyl-$\beta$-picrylhydrazyl.** An inhibitor, $\alpha,\alpha$-diphenyl-$\beta$-picrylhydrazyl (DPPH), J. T. Baker Chemical Co., was recrystallized repeatedly from chloroform (mp 139°).

(B) **Apparatus.** Infrared spectra were taken on a Perkin-Elmer recording spectrophotometer, Model 21. The oxidation cell used and various experimental details have been given in earlier works.[4-6]

(C) **Procedure.** A film of APP containing certain amounts of cobalt(III) acetylacetonate and DPPH was cast on an optical sodium chloride disk (25 × 5 mm) from solutions in carbon tetrachloride. The films (*ca.* 2.5 mils) on the disks were assembled in the oxidation cell and attached to the spectrophotometer. Mixtures of oxygen and nitrogen containing 25, 50, 75, and 100% oxygen were used. Reaction temperatures ranged from 110 to 130°. The catalyst and inhibitor contents were varied from (6.0 to 60.0) $\times 10^{-8}$ mol and from (1.0 to 15.0) $\times 10^{-8}$ mol, respectively, per 7.5 mg of APP. APP concentrations were changed by admixture with polyisobutylene[5] and varied from 24.6 to 100 wt %.

Infrared spectra of the carbonyl region were recorded as a function of reaction time for different concentrations of DPPH, cobalt(III) acetylacetonate, APP, and oxygen, and for different temperatures.

## Results and Discussion

Rates of initiation were determined by using the well-known inhibitor method.[11] Thus we may write

$$R_i = -n(d[AH]/dt) = n[AH]_0/t_i \quad (1)$$

where $R_i$ is the rate of initiation, $n$ is the stoichiometric factor (a number of radicals terminated by one molecule of inhibitor), [AH] and $[AH]_0$ represent an inhibitor concentration at any time $t$ and initially, respectively; and $t_i$ is the induction time. In eq 1 it is assumed that the rate of disappearance of inhibitor is constant.

We can also write for the rate of initiation, using our previously proposed scheme[6]

$$R_i = fk_d[O_2][RH][cat.] \quad (2)$$

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(1) (a) Stevens Institute of Technology; (b) Picatinny Arsenal.

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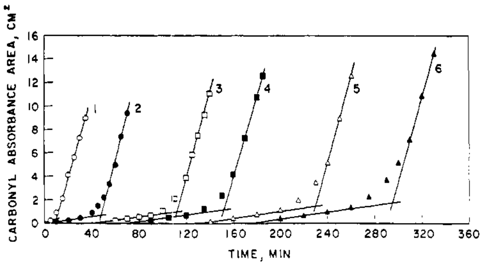

Figure 1. Carbonyl absorbance area *vs.* time; temperature = 120°, pure oxygen, and [Co(III)] = $3 \times 10^{-7}$ mol/7.5 mg of APP for various concentrations of $\alpha,\alpha$-diphenyl-$\beta$-picrylhydrazyl: (1) $1 \times 10^{-8}$, (2) $3 \times 10^{-8}$, (3) $6 \times 10^{-8}$, (4) $9 \times 10^{-8}$, (5) $1.2 \times 10^{-7}$, (6) $1.5 \times 10^{-7}$ mol.

Further, from Figure 1, the catalyst concentration does not appear to vary much during the induction period, so that $[\text{cat.}] \approx [\text{cat.}]_0$. Then, upon combining eq 1 and 2

$$1/t_i = F[\text{cat.}]_0/n[\text{AH}]_0 \qquad (3)$$

where $f$ is an efficiency factor, $k_d$ the rate constant for the initiation process, $[\text{O}_2]$ the oxygen concentration, [RH] the substrate concentration, [cat.] the catalyst concentration (*e.g.*, cobalt(III) acetylacetonate), and $F = fk_d[\text{O}_2][\text{RH}]$.

The effect of the addition of DPPH to the cobalt(III) acetylacetonate catalyzed oxidation of APP was studied in detail to get information about the initiation step. The addition of DPPH produced an induction period, $t_i$, during which practically no carbonyl could be detected. The presence of a significant amount of peroxide can, therefore, be ruled out. The only major source of free radicals, consumed by DPPH, is the initiation reaction. Figure 1 shows plots of carbonyl absorbance area *vs.* time as a function of inhibitor concentration. Tangents were drawn to the oxidation curves at an early stage in the run and the intersection of the tangents with the straight lines drawn through the points taken late in the run, after the oxidation rate assumed its uninhibited value, gave extrapolated zero-order induction times.[12]

It is noted from Figure 1 that the length of induction time increases with increasing inhibitor concentration. The maximum reaction rate reached after the end of the induction period did not seem to be affected by the amount of DPPH added initially to the system. This also indicates that [cat.] ≈ constant during the initiation period.

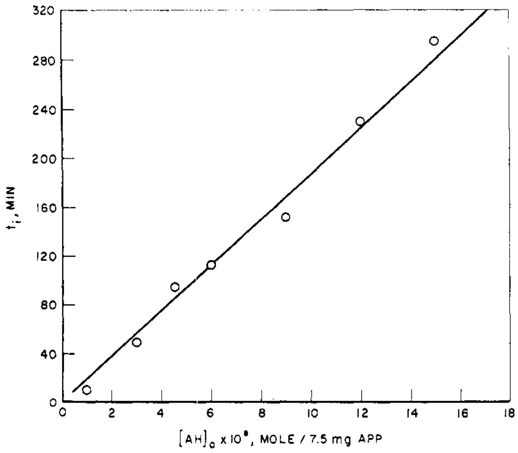

Figure 2. Variations of length of induction period with concentration of $\alpha,\alpha$-diphenyl-$\beta$-picrylhydrazyl; temperature = 120°, pure oxygen, [Co(III)] = $3 \times 10^{-7}$ mol/7.5 mg of APP.

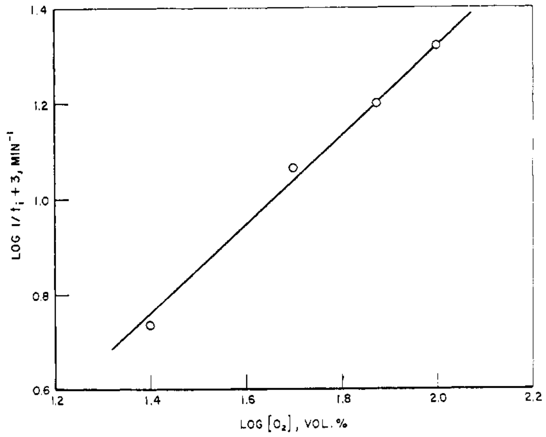

Figure 3. Dependence of induction period on oxygen concentration; temperature = 120°, [Co(III)] = $3 \times 10^{-7}$ mol, [AH] = $3 \times 10^{-8}$ mol/7.5 mg of APP.

From eq 3, when temperature and concentrations of polymer, oxygen, and catalyst are maintained constant, the induction period should be directly proportional to the initial inhibitor concentration, $[\text{AH}]_0$, as shown in Figure 2. In this regard it may be mentioned that changes in oxygen solubility with temperature should be small in the temperature range used due to the *generally* low activation energies for solubility of various gases in polymers. This linearity and the fact that the maximum rates are not influenced by the presence of inhibitor imply that the fraction of catalyst consumed during the initiation period is relatively small, and that practically no side reactions are occurring, *e.g.*, between inhibitor and oxygen or catalyst, respectively. Further, the maximum rates obtained ($\rho_{\max} = 0.36$ cm²/min) from Figure 1 were similar in value to that obtained during studies of catalyzed oxidation of APP without an inhibitor ($\rho_{\max} = 0.371$ cm²/min).[6] This further supports the occurrence of no side reactions. Accordingly, this initiation process can be treated as a normal process similar to that found in liquid-phase initiation of free radicals.

A series of experiments was carried out to determine relationships between the length of induction time, $t_i$, and the other variables of our system. From eq 3, when temperature

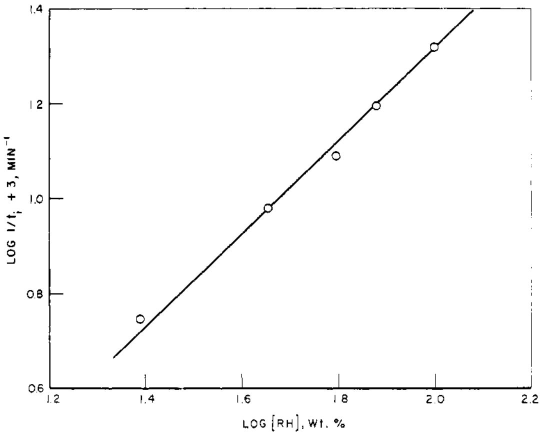

Figure 4. Dependence of induction period on polypropylene concentration; temperature = 120°, pure oxygen, [Co(III)] = $3 \times 10^{-7}$ mol, [AH] = $3 \times 10^{-8}$ mol/7.5 mg of APP.

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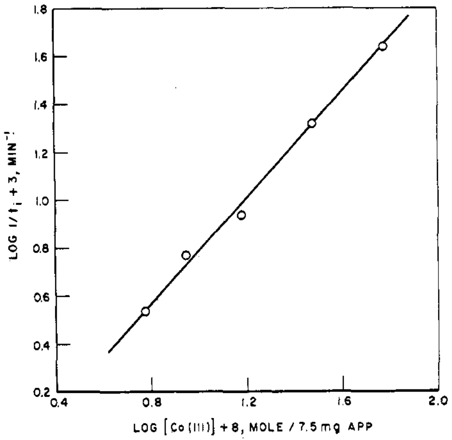

Figure 5. Dependence of induction period on the concentration of cobalt(III) acetylacetonate; *temperature* = 120°, *pure oxygen*, [AH] = 3 × $10^{-8}$ mol/7.5 mg of APP.

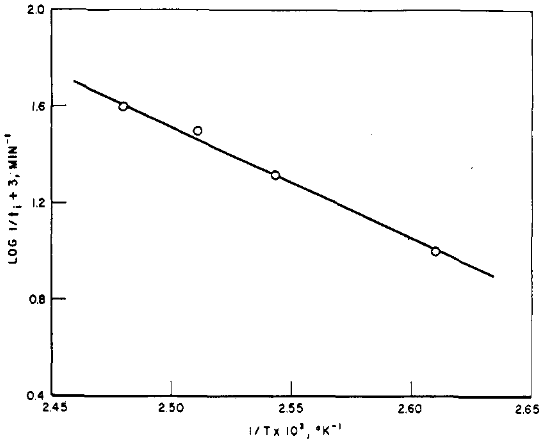

Figure 6. Plot of log $1/t_i$ *vs.* reciprocal temperature; pure oxygen, [Co(III)] = 3 × $10^{-7}$ mol, [AH] = 3 × $10^{-8}$ mol/7.5 mg of APP.

and concentrations of polymer, catalyst, and inhibitor are kept constant, a plot of log $1/t_i$ *vs.* log $[O_2]$ should afford the kinetic dependence of the initiation rate, $R_i$, upon oxygen concentration; *cf.* Figure 3. This was found to be 0.94. Similarly, a plot of log $1/t_i$ *vs.* log [RH], keeping other variables constant, gave a kinetic order of 1.05; *cf.* Figure 4. In a similar manner, the order with respect to the catalyst concentration was found to be 1.09; *cf.* Figure 5.

From eq 3 it can be seen that when the concentrations are maintained constant, an Arrhenius plot of log $1/t_i$ *vs.* reciprocal temperature, $1/T$, should afford an activation energy for the initiation step, $E_d$. Thus, $E_d$ was found to have a value of 21 kcal/mol; *cf.* Figure 6. It may be noted here that assuming a C–H bond energy of 90 kcal/mol, the activation energy for the uncatalyzed initiation reaction.

$$RH + O_2 \longrightarrow R\cdot + HO_2\cdot \qquad (4)$$

should be approximately 45 kcal/mol.[13]

A rough estimate of $k_d$ value at 120° (Figure 2) was made as follows. From diffusion measurements, the solubility of oxygen at 1 atm of pressure in highly amorphous polyethylene was estimated to be about $10^{-3}$ *M*. This value was used for APP. Also, using the stoichiometric factor for DPPH,[12] $n = 2, f = 1$, it was estimated from eq 3 and Figure 2 that $k_d(120°) \approx 0.2\ l.^2\ mol^{-2}\ min^{-1}$.

The initiation process directly involves all three components of the reaction: oxygen, substrate, and catalyst. Therefore, the initiation reaction cannot be a simple interaction between metal and oxygen or metal and polymer. From the preceding, one of several initiation mechanisms may be

$$\text{cat.} + RH \rightleftharpoons [\text{cat.}\cdots H\cdots R] \qquad (5a)$$

$$[\text{cat.}\cdots H\cdots R] + O_2 \longrightarrow \text{cat.} + R\cdot + HO_2\cdot \qquad (5b)$$

This initiation mechanism is in agreement with the scheme proposed for the metal salt catalyzed autoxidation of polyolefins.[5–9] Further, Osawa and coworkers[14] have postulated a similar step as shown in eq 5a, *i.e.*

$$\text{cat.} + RH \longrightarrow \text{cat.(H)} + R\cdot \qquad (6)$$

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