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Ethylene Polymerization with Phillips Catalyst Co-catalyzed with Al(i-Bu)$_3$

TAE W. WOO AND SEONG I. WOO[1]

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, Korea

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The kinetics of ethylene polymerization with $CrO_3/SiO_2/Al(i\text{-}Bu)_3$ has been investigated in the range of temperatures between 323 and 353 K and in the range of pressures between 116.7 and 268.7 psia. The effects of aluminum alkyl on the formation and the deactivation of active sites are discussed. The rate of polymerization is considered to occur between adsorbed monomer and an active center, and the change in the polymerization rate at the initial period is described by formation of active sites from the interaction of adsorbed aluminum alkyl with preactive sites. Decay of the polymerization rate, which was independent of the monomer concentration, is ascribed to the excess aluminum alkyl that could poison the active sites by the Langmuir–Hinshelwood mechanism. Activation energy obtained from the maximum polymerization rates between 323–353 K was 8.8 kcal/mol. An apparent negative activation energy was obtained above 343 K and is ascribed to the destruction of active sites.

INTRODUCTION

Conventional Phillips catalyst, CrO_3/SiO_2, has an induction period in the polymerization of ethylene when CrO_3/SiO_2 is not prereduced with a reducing agent. The induction period is strongly dependent on the polymerization temperature. Below 333 K polymerization does not occur. At higher temperature, the induction period becomes shorter and disappears at 423 K (*1*). The addition of aluminum alkyls to the polymerization system greatly changes the kinetic profile; the induction period is eliminated and the polymerization rate reaches its maximum value very rapidly. This phenomenon was reported earlier by other authors (*2–5*) and in a few patents (*6, 7*). The polymer produced showed the main characteristics of Phillips polyethylene (*5*).

However, the effect of aluminum alkyl on the CrO_3/SiO_2 catalyst has not been fully understood until now. This report will discuss the aluminum alkyl effect on the kinetics of ethylene polymerization with Phillips catalyst.

EXPERIMENTAL

Materials

Ethylene (polymer grade, Yukong, Ltd., Korea) and nitrogen of extra-pure grade were further purified with Fisher RIDOX columns and a 5A/13X molecular sieve. *n*-Hexane of extra-pure grade (Duksan, Ltd., Korea) was passed through the molecular sieve column and further dried by refluxing over sodium metal/benzophenone in a nitrogen atmosphere. Triisobutylaluminum, Al(i-Bu)$_3$, diluted in *n*-hexane (Aldrich, U.S.A.) was used without further purification. Chromium(VI) oxide (99.99%) was purchased from Kokusan Chemical, Ltd., Japan. Silica gel, large pore (No. 414-7420) was purchased from Strem Chemical, Inc., U.S.A. The surface area is 350 m^2/g and the pore volume is 2.7 ml/g. The average pore radius is about 15 nm.

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[1] To whom all correspondence should be addressed.

0021-9517/90 $3.00

Catalyst Preparation

Catalyst was prepared using an impregnation method. Chromium(VI) oxide dissolved in water was impregnated into 10 g of silica gel and dried in a rota-evaporator at 308 K for 3 hr. This impregnated catalyst (Cr loading = 1 wt%) was dried in an oven at 393 K for 36 hr and stored in a desiccator before calcination. To activate the catalyst, about 3 g of impregnated catalyst was fluidized in a dry air stream at 1123 K for 2 hr. A quartz tube with sintered glass frit was used to support the sample and heated to 1123 K at a rate of 5.2 K/min with a dried air flow rate of 320 cm^3/sec through the bed. After calcination, catalyst was purged with nitrogen at 623 K for 1 hr and stored in a glovebox before use.

Polymerization

Slurry polymerization was carried out in a 1-liter Parr reactor (Series 4520) with two turbine type impellers, a spiral cooling coil, and a deep tube to introduce monomer under constant pressure of ethylene. A schematic diagram of the polymerization reactor system is shown in Fig. 1.

A glass ampoule containing catalyst was installed in the reactor. After evacuation and purge with nitrogen several times at 383 K, a prescribed amount of $Al(i\text{-}Bu)_3$ and 500 ml of *n*-hexane were introduced into the reactor under nitrogen stream. Then ethylene was introduced at the polymerization temperature. When ethylene was saturated into the diluent, *n*-hexane, polymerization was started by breaking the glass ampoule containing the prescribed amount of catalyst.

The polymerization mixture was agitated with a stirrer at 800 rpm in order to avoid a mass transfer resistance through the gas–liquid interface. The temperature of polymerization was controlled within ±1.0 K. The rate of polymerization every 0.02 sec from the rate of ethylene consumption was measured with a mass flow meter (Model 5858D, Brooks Instrument Division) connected to a personal computer through an A/D converter. Polymer yield calculated from the consumption rate of ethylene agreed within ±2.5% with the yield measured by the weight of polymer produced.

RESULTS AND DISCUSSION

When $Al(i\text{-}Bu)_3$ is added to the polymerization reactor, polymerization begins without any induction period. The rate reaches a maximum within 10 min. Figure 2 shows the typical curves of polymerization rate profile. Conventional CrO_3/SiO_2 catalysts have a long induction period. The polymerization rate increases slowly during the initial first hour to a steady-state value (*1*, *2*).

Determination of Amount of Aluminum Alkyl as a Scavenger

To determine the amount of $Al(i\text{-}Bu)_3$ consumed as a scavenger for our high-pressure polymerization reactor system, polymerizations were carried out with CO-reduced catalysts. Polymerization did not occur when a concentration of $Al(i\text{-}Bu_3)$ less than 0.765 mmol/liter was used. This was assumed to be the amount of $Al(i\text{-}Bu)_3$ required to scavenge impurities in our polymerization system.

Absence of External Diffusion Resistance

Polymerizations were carried out with various amounts of catalysts. As shown in Table 1, productivities per gram catalyst with different amounts of catalyst are nearly constant at the same concentration of aluminum alkyl [A'], which shows that external diffusion resistance is negligible in our experiment. Despite different ratios of aluminum alkyl to catalyst, the polymerization rate profiles are nearly identical. This was also discussed earlier by McKenzie *et al.* in Ziegler–Natta catalysis (*8*).

The Role of Aluminum Alkyl as a Co-catalyst

After calcination, the oxidation state of chrome supported on silica has been reported as 6+ (*9–12*), which can be reduced to a lower oxidation state and alkylated by

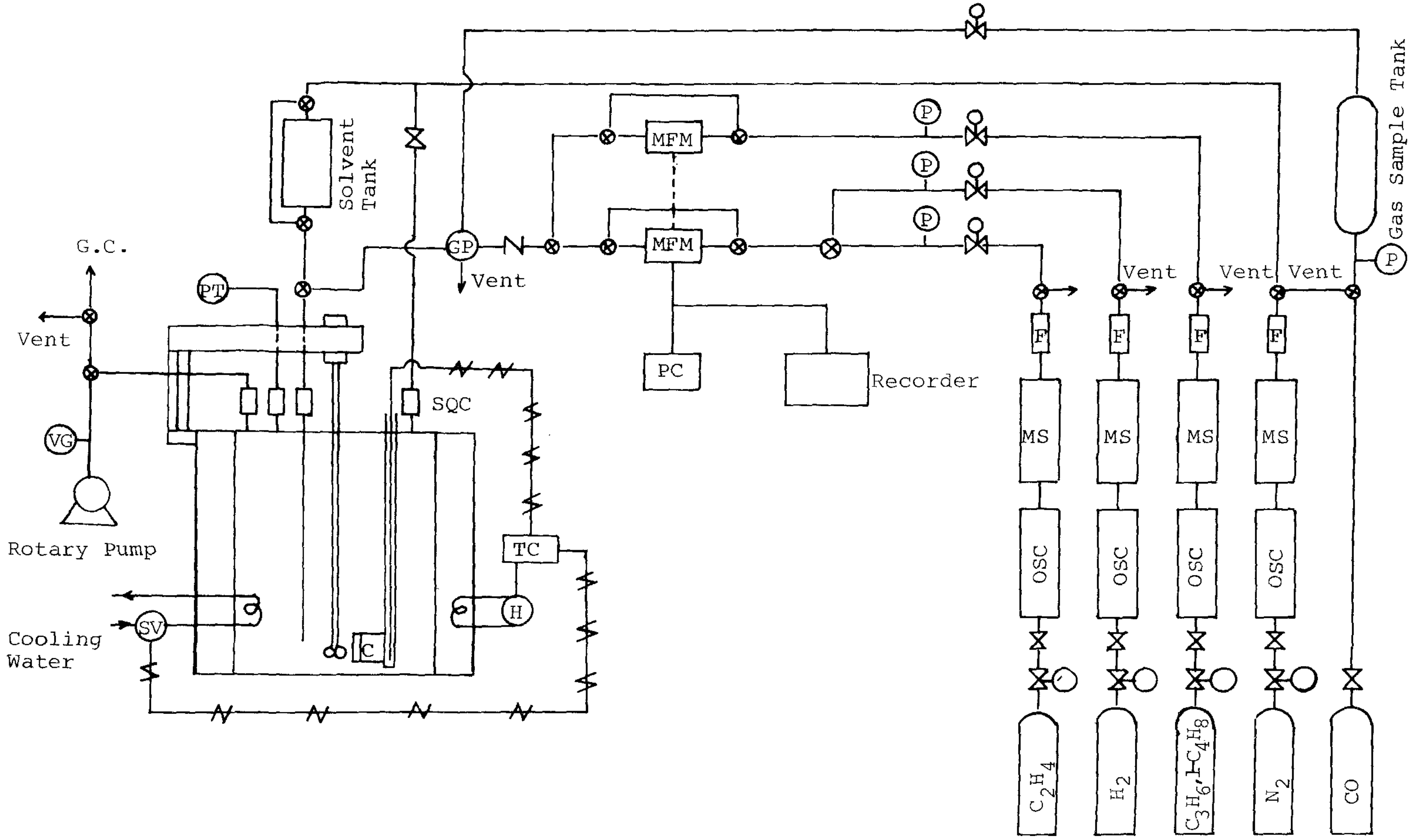


FIG. 1. High-pressure polymerization unit: (C) catalyst vial; (F) filters; (H) heater; (MFM) mass flow meter; (MS) molecular sieves; (OSC) oxygen scavenging columns; (PT) pressure transducer; (SQC) series quick connector; (SV) solenoid valve; (TC) temperature controller; (VG) vacuum gauge.

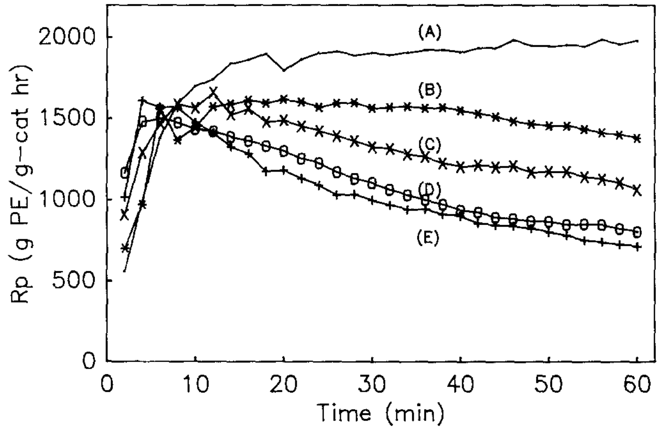
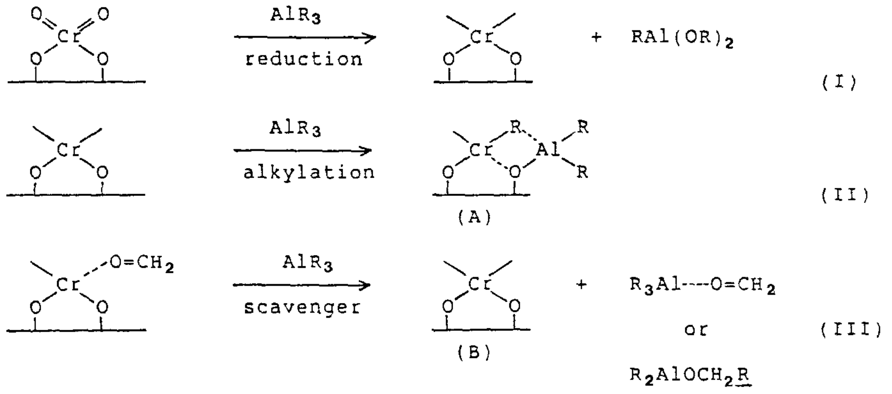


FIG. 2. Polymerization rate profiles with different amounts of Al(i-Bu)$_3$. Polymerization conditions: P_E = 166.7 psia, T = 70°C, and [Al(i-Bu)$_3$] in millimoles per liter; (A) 1.071, (B) 1.428, (C) 2.04, (D) 3.37, (E) 4.59.

the aluminum alkyl compound (*2–5*). Aluminum alkyls can scavenge aldehydes and ketones which are produced during the reduction by ethylene (*13*). This is comparable with the fact that pyridine (Py) coordinated to $TiCl_3$ as $TiCl_3 \cdot 3Py$ was reported to be removed by treatment with a Lewis acid such as $AlEt_2Cl$ (*14*). Hence, Al(i-Bu)$_3$ can also scavenge electron donors such as aldehydes and ketones. Interaction of aluminum alkyl with surface chrome species can be proposed as follows:



Our polymerization data with Al(i-Bu)$_3$ as a co-catalyst show that there is no induction period. The reason for the absence of induction period when small amounts of aluminum alkyl compounds are added might be the instantaneous formation of active polymerization centers (A) through the reduction and alkylation as shown in (I) and (II) (*2*). Another reason may be the easy removal of polar compounds (B) formed by the reduction of Cr(VI) with ethylene during the initiation step (*1, 2*).

As shown in Fig. 2, the more Al(i-Bu)$_3$ added, the more rapidly the reaction reaches the maximum rate of polymerization.

TABLE 1

Productivity with Various Amounts of Catalyst (Polymerization Conditions: T = 343 K, $[M]^a$ = 1.1786 mol/liter)

Catalyst (g)	$[A]^b$ (mmol/liter)	$[A']^b$ (mmol/liter)	$[A']/[\mathrm{Cr}]^c$ (mol ratio)	Yield (g PE)	Productivity (g PE/g cat. hr)
0.02	1.428	0.663	86.2	30.35	1518[d]
0.045	1.428	0.663	38.2	66.11	1475[d]
0.070	1.428	0.663	24.6	101.5	1450[d]
0.02	3.366	2.601	338.1	22.12	1106[e]
0.046	3.366	2.601	147.0	54.63	1178[e]

[a] $[M]$, concentration of ethylene in liquid phase.

[b] $[A]$, total amount of Al(i-Bu)$_3$ in the reactor; $[A'] = [A] - 0.765$ (amount of aluminum alkyl as a scavenger).

[c] Impregnated Cr is assumed to be totally converted to preactive sites after calcination.

[d,e] Other kinetic characteristics, change of polymerization rate at the initial period and decay rate constant, are nearly the same as those shown in Tables 2 and 5.

Effect of Aluminum Alkyl Concentration on the Initial Polymerization Rate

When $\mathrm{CrO_3/SiO_2}$ was reduced with CO (*3*, *15*), aluminum alkyl, or aluminoxane (*3*), several types of $\mathrm{Cr^{2+}/SiO_2}$, depending on the coordination with surface silanol or siloxane, were reported. If aluminum alkyl is adsorbed on the preactive sites, $\mathrm{Cr^{6+}/SiO_2}$, to reduce $\mathrm{Cr^{6+}}$ to $\mathrm{Cr^{2+}}$ and to alkylate the reduced sites and if the polymerization rate is proportional to the amount of adsorbed monomer and the polymerization center, the polymerization rate expression can be obtained with the following mechanism. Here two types of active polymerization center were assumed; one is formed by contact with ethylene monomer and the other is formed by contact with aluminum alkyl.

Polymerization center formation by aluminum alkyl,

$$l + \mathrm{Al}R_3\ (A) \underset{k_{-\mathrm{A}}}{\overset{k_{\mathrm{A}}}{\rightleftharpoons}} l_{\mathrm{A}} \xrightarrow{k_1} C^*,$$

$$K_{\mathrm{A}} = k_{\mathrm{A}}/k_{-\mathrm{A}}. \qquad (1)$$

Polymerization center formation by monomer,

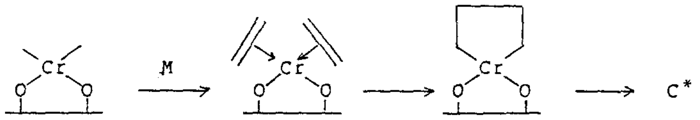
$$l + \mathrm{C_2H_4}\ (M) \underset{k_{-\mathrm{M}}}{\overset{k_{\mathrm{M}}}{\rightleftharpoons}} l_{\mathrm{M}} \xrightarrow{k_2} C_{\mathrm{r,M}},$$

$$K_{\mathrm{M}} = k_{\mathrm{M}}/k_{-\mathrm{M}} \qquad (2)$$

$$C_{\mathrm{r,M}} + M \xrightarrow{k_3} C^*, \qquad (3)$$

where l is the $\mathrm{Cr^{6+}}$ site, l_{A} is the site adsorbed by aluminum alkyl, l_{M} is the site adsorbed by monomer, C^* is the polymerization active center, and $C_{\mathrm{r,M}}$ is the reduced site by monomer.

The mechanism of active polymerization center formation by ethylene was suggested to involve the formation of cyclobutane complex which is believed to be a slow reaction as follows (*16*):



Thus polymerization center formation via Eqs. (2) and (3) can be ignored in the presence of Al(i-Bu)$_3$ because the induction period of the polymerization with a catalyst activated by aluminum alkyl is not present. Applying the Langmuir–Hinshelwood ad-

TABLE 2

Effect of Al(i-Bu)$_3$ Concentration on the Change in Polymerization Rate at the Initial Period (Polymerization Conditions: 343 K, $[M]$ = 1.1786 mol/liter)

Catalyst (g)	$[A]$ (mmol/liter)	$[A']$ (mmol/liter)	dR_p/dt (Kg PE/g cat. hr^2)
0.07	1.071	0.306	16.8
0.02	1.428	0.663	19.5
0.045	1.428	0.663	21.0
0.07	1.428	0.663	21.6
0.02	1.632	0.867	24.9
0.02	2.04	1.275	27.3
0.046	3.366	2.601	35.2
0.02	3.366	2.601	36.0
0.07	4.590	3.825	30.6

sorption isotherm for the case of competitive adsorption of A and M on the Cr^{6+} site, θ_A and θ_M can be obtained as follows:

$$\theta_A = \frac{K_A[A]'}{1 + K_A[A]' + K_M[M]} \qquad (4)$$

$$\theta_M = \frac{K_M[M]}{1 + K_A[A]' + K_M[M]}. \qquad (5)$$

Assuming only one type of active polymerization center is formed by aluminum alkyl, the rate of the formation of active polymerization centers can be expressed as:

$$d[C^*]/dt = k_1\theta_A[l_t], \quad \text{where } l_t = l + l_M + l_A \qquad (6)$$

Substituting Eqs. (4) and (5) into Eq. (6),

$$\frac{d[C^*]}{dt} = \frac{k_1 K_A[A]'[l_t]}{1 + K_A[A]' + K_M[M]}. \qquad (7)$$

When polymerization centers (C^*) contact with the adsorbed monomer, polymerization begins instantaneously. The rate of propagation can be expressed as

$$R_p = k_p\theta_M[C^*] \qquad (8)$$

$$dR_p/dt = k_p\theta_M d[C^*]/dt$$

$$= k_p \frac{k_1 K_A[A]' K_M[M]}{(1 + K_A[A]' + K_M[M])^2}[l_t] \qquad (9)$$

$$= \frac{k_{p,i}[A]'[M]}{(1 + K_A[A]' + K_M[M])^2}, \quad \text{with } k_{p,i} = k_p k_1 K_A K_M[l_t] \qquad (10)$$

K_A is usually much larger than K_M and when the polymerization is run at constant pressure of ethylene, the following expression can be obtained:

$$dR_p/dt = \frac{k'_{p,i}[A]'}{\{1 + K_A[A]'\}^2]}, \quad \text{with } k'_{p,i} = k_p k_1 K_A K_M[l_t][M]. \qquad (11)$$

If $[A]'$ is constant,

$$dR_p/dt = \frac{k''_{p,i}[M]}{\{1 + K_A[A]'\}^2}, \quad \text{with } k''_{p,i} = k_1 k_p K_A K_M[l_t][A]'. \qquad (12)$$

Polymerization rate profiles with different amounts of Al(i-Bu)$_3$ are shown in Fig. 2. As the amount of Al(i-Bu)$_3$ increased, the average activity decreased and the rate profile changed from nondecaying type to decaying type.

The change in the polymerization rate at the initial period is hard to determine experimentally. Instead, we determined the change in polymerization rate during the first 2 min. Those data are tabulated in Table 2. Figure 3 shows that the initial change in polymerization rate increases as the concentration of Al(i-Bu)$_3$ increases, but decreases above 3.5 mmol/liter.

The plot of $([A']/(dR_p/dt))^{0.5}$ vs $[A']$, by

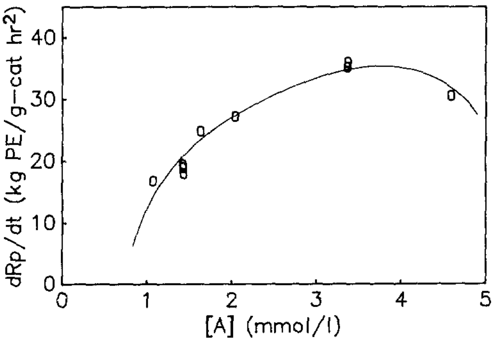


FIG. 3. Initial change in polymerization rate with different amounts of aluminum alkyl. Same polymerization conditions as those in Fig. 2.

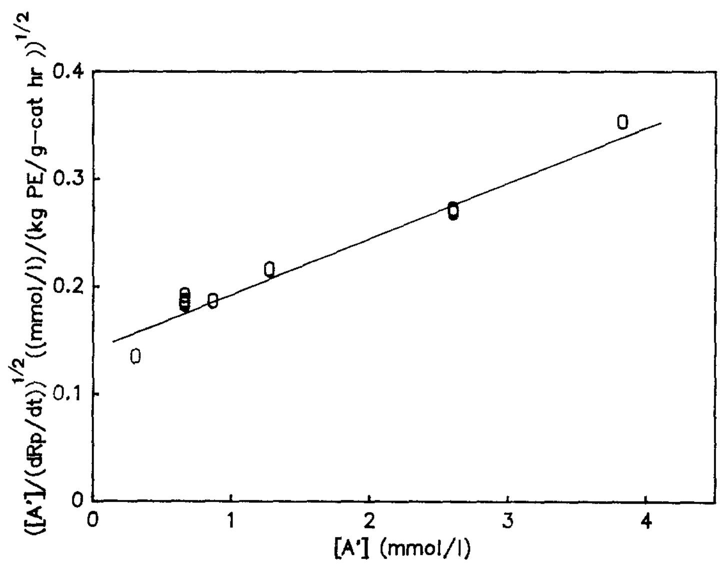


FIG. 4. Linear plot of $\{[A']/(dR_p/dt)\}^{0.5}$ vs $[A']$. Same polymerization conditions as those in Fig. 2.

Eq. (11) ($[A'] = [A] - S_1$, where S_1 is the amount of aluminum alkyl that is used for scavengers; in our polymerization system S_1 is 0.765 mmol/liter), is shown in Fig. 4. From the slope and intercept, the K_A value, 373 liter/mol at 343 K and 166.7 psia of ethylene pressure, is obtained. It is noteworthy that if the initial change in polymerization rate is governed by Eq. (11), the maximum value of the change in polymerization rate is obtained at $A' = 1/K_A = 2.68$ mmol/liter and the corresponding value of A is 3.45 mmol/liter as shown in Fig. 3.

Effect of Monomer Concentration on the Change in Polymerization Rate at the Initial Period

The effect of monomer pressure on the change in polymerization rate is tabulated in Table 3. Figure 5 shows that the change in the polymerization rate is proportional to the monomer concentration in the range of

TABLE 3

Effect of Monomer Concentration on the Change in Polymerization Rate at the Initial Period (Polymerization Conditions: T = 343 K, $[A]$ = 2.04 mmol/liter)

Pressure (psia)[a]	$[M]$[b] (mol/liter)	dR_p/dt (Kg PE/g cat. hr^2)
116.7	0.757	16.64
166.7	1.179	24.60
218.7	1.633	31.50
267.7	2.121	37.20

[a] 1 psia = 6.893 × 10^3 Pa.

[b] Monomer concentration calculated by Redlich–Soave–Kwong equation.

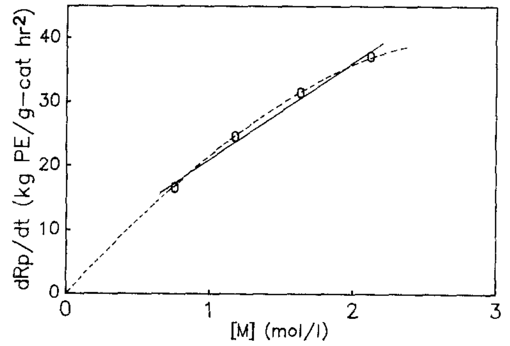


FIG. 5. Effect of monomer concentration on the initial change in polymerization rate. T = 70°C, $[Al(i\text{-}Bu)_3]$ = 2.04 mmol/liter. (—) Linear plot by Eq. (12). (---) Curve fitting by Eq. (10).

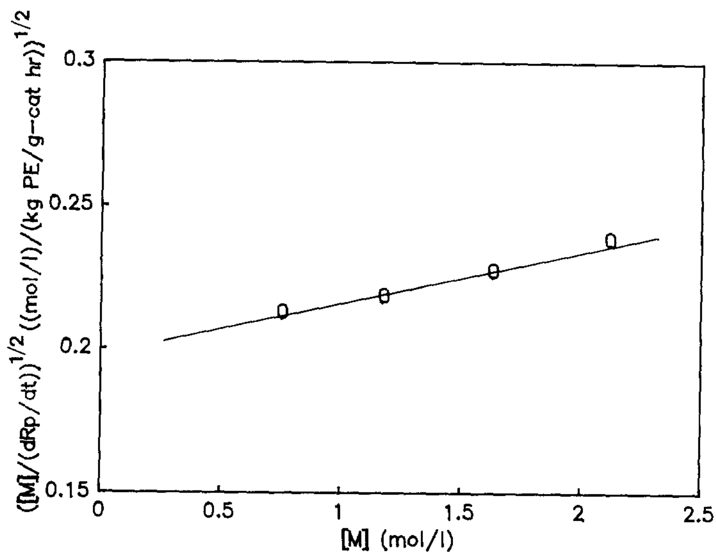


FIG. 6. Linear plot of $\{[M]/(dR/dt)\}^{0.5}$ vs $[M]$ by Eq. (10). Same polymerization conditions as those in Fig. 5.

monomer concentration from 0.757 to 2.121 mol/liter according to Eq. (12). To determine the K_M value, $([M]/dR_p/dt))^{0.5}$ against $[M]$ is plotted in Fig. 6, by Eq. (10). The linear relationship is good enough to determine a K_M value. From the slope and intercept and K_A value determined previously, a K_M value of 0.1405 liter/mol is determined. K_M is much smaller than K_A (373 liter/mol), which is consistent with our assumption in the proposed mechanism.

TABLE 4

Effect of Polymerization Temperature on the Change in Polymerization Rate at the Initial Period (Polymerization Conditions: $[A]$ = 2.04 mmol/liter, $[M]$ = 1.1786 mol/liter)

Catalyst (g)	T (K)	dR_p/dt (Kg PE/g cat. hr^2)
0.07	323	10.5
0.015	333	18.0
0.02	333	19.5
0.07	343	27.3
0.02	353	36.0
0.02	353	42.0

Effect of Temperature on the Change in Polymerization Rate at the Initial Period

As shown in Fig. 7, the change in polymerization rate at the initial period increases as the temperature of polymerization increases. The change in polymerization rate with various temperatures is tabulated in Table 4. From the Arrhenius plot in Fig. 8, an activation energy of change in polymerization rate at the initial period ($E_{p,i}$), 9.8 kcal/mol, could be obtained.

Effect of Aluminum Alkyl Concentration on the Deactivation

Figure 2 shows that the rate of polymerization begins to decrease after its maximum point when the concentration of $Al(i\text{-}Bu)_3$ is higher than 1.07 mmol/liter. The more $Al(i\text{-}Bu)_3$ is added, the faster the rate of decrease is. This phenomenon could be due to the excess aluminum alkyl that could play a role as a deactivator or/and terminator. Decay in rate of propylene polymerization is one of the prominent characteristics of Ziegler–Natta catalysis.

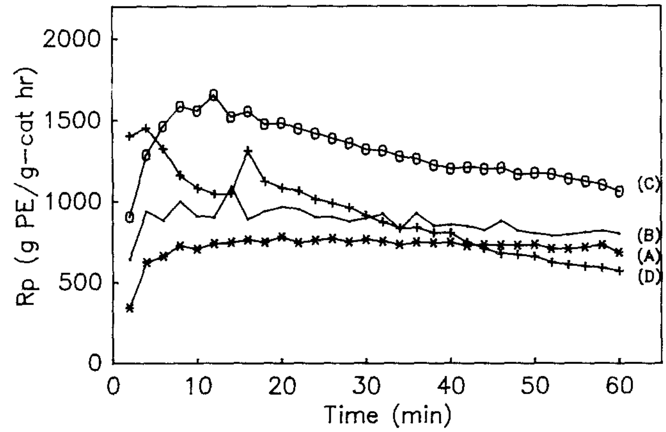
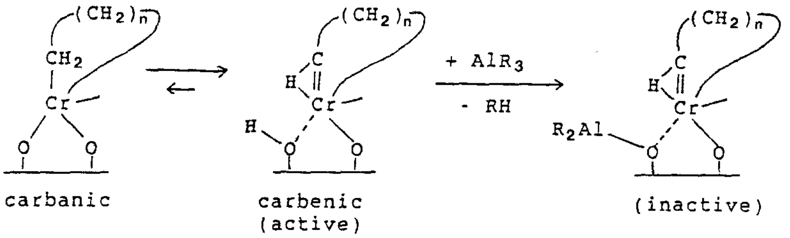


FIG. 7. Polymerization rate profiles with different temperatures. $[A] = 2.04$ mmol/liter, $[M] = 1.1786$ mol/liter. Temperature in degrees K; (A) 323, (B) 333, (C) 343, (D) 353.

$AlEt_2Cl$ co-catalyst can act as a poison in $TiCl_3/AlEt_2Cl$ catalysis (*17*). Deactivation of active polymerization centers can occur due to the reduction of Ti^{3+} to Ti^{2+} in $TiCl_3/AlEt_3$ catalysis (*18*).

It was suggested that the activities of CrO_3/alumina and CrO_3/aluminophosphate catalysts without aluminum alkyl decreased due to the decrease in the number of active sites (*1, 2*). The mechanism of the deactivation in $CrO_3/SiO_2/Al(i\text{-}Bu)_3$ is not known yet. One possibility is that excess aluminum alkyl over-reduces Cr^{2+} to Cr^{1+} or Cr^0. The true reduction of Cr^{2+}/SiO_2 to Cr^{1+} or Cr^0 by CO above 573 K was reported to be thermodynamically highly unfavorable (*19*). However, possibility of over-reduction by $Al(i\text{-}Bu)_3$ cannot be ruled out because $Al(i\text{-}Bu)_3$ is a strong reducing agent. During polymerization, ethylene physically adsorbs on hydroxyl sites of silica and may easily relocate onto adjacent active polymerization centers (*20*). Hence the other possibility is that the propagation rate can be much lowered due to a decrease in surface hydroxyls, because aluminum alkyl can diminish surface hydroxyls (*21*). Another possibility is that aluminum alkyl may interfere with a polymerization cycle. Recently the structure of the active polymerization center was suggested to be cyclic in form and a alkylidenic (carbenic) configuration was assumed to be formed by the reversible transfer of hydrogen to the nearby oxygen (*16, 22*). If hydrogen atoms attached to oxygen atoms react with aluminum alkyl, inactive polymerization sites may be formed as follows:



If we assume that excess aluminum alkyl deactivates polymerization active centers, the rate of decrease in the number of active sites can be expressed as

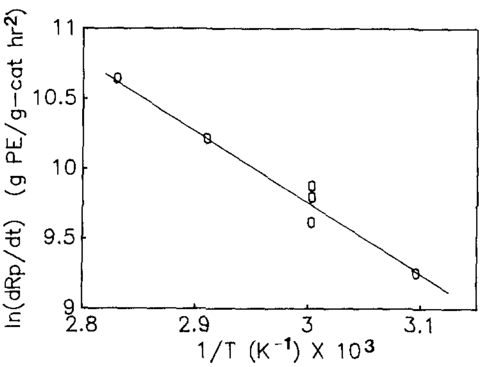


FIG. 8. Arrhenius plot of change in polymerization rate at the initial period. $[A] = 2.04$ mmol/liter, $[M] = 1.1786$ mmol/liter.

$$d[C^*]/dt = -k_d\theta_A[C^*] = \frac{-k_dK_A[A''][C^*]}{(1 + K_A[A''] + k_M[M])}, \qquad (13)$$

where $[A''] = [A] - S_2$ and S_2 is the amount of aluminum alkyl used as scavenger, reducing, and alkylating agent.

If $K_A \gg K_M$,

$$dC^*/dt = -k_d'[C^*],$$

where

$$k_d' = k_dK_A[A'']/(1 + K_A[A'']) \qquad (14)$$

The deactivation of the polymerization rate can be expressed as

$$dR_p/dt = k_p\theta_M d[C^*]/dt. \qquad (15)$$

Substituting Eq. (14) into Eq. (15), the following expression can be obtained:

$$dR_p/dt = -k_d'R_p. \qquad (16)$$

Log R_p against time is plotted in Fig. 9, which shows a good linear relationship. From the slope in Fig. 9, the deactivation rate constant, k_d', can be obtained.

Deactivation rate constants (min^{-1}) with various concentrations of Al(i-Bu)$_3$ are tabulated in Table 5. As shown in Fig. 10, the deactivation rate constant approaches a limiting value at higher Al(i-Bu)$_3$ concentration. The value $1/k_d'$ is plotted against $1/[A'']$ using Eq. (14), ($A'' = A - S_2$, where $S_2 = 1.07$ mmol/liter which is the amount of aluminum alkyl sufficient for scavenger, reducing, and alkylating agents). From the slope and intercept in Fig. 11, K_A is calculated to be 421 liters/mol at 343 K and 166.7 psia of ethylene pressure. This value is close to the value of K_A, 373 liters/mol obtained from Eq. (11).

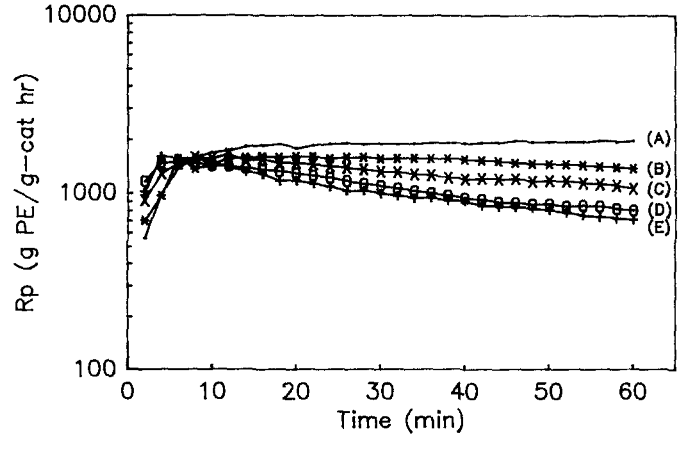


FIG. 9. Logarithmic plot of polymerization rate vs polymerization time; same polymerization conditions as those in Fig. 2. [Al(i-Bu)$_3$] in millimoles per liter; (A) 1.071, (B) 1.428, (C) 2.04, (D) 3.37, (E) 4.59.

TABLE 5

Effect of Triisobutyl Aluminum Concentration on the Decay Rate Constants (Polymerization Conditions: T = 70°C, $[M]$ = 1.1786 mol/liter)

Catalyst (g)	$[A]$ (mmol/liter)	$[A'']$ (mmol/liter)	$[A'']/[Cr]$ (mol ratio)	k_d' (min^{-1})
0.07	1.071	0.0	—	—
0.02	1.428	0.257	14.8	3.3
0.045	1.428	0.257	9.5	3.5
0.02	1.632	0.561	72.9	6.5
0.02	2.04	0.969	126.0	8.5
0.046	3.366	2.295	129.7	12.2
0.02	3.366	2.295	298.3	12.4
0.07	4.590	3.519	130.7	13.2

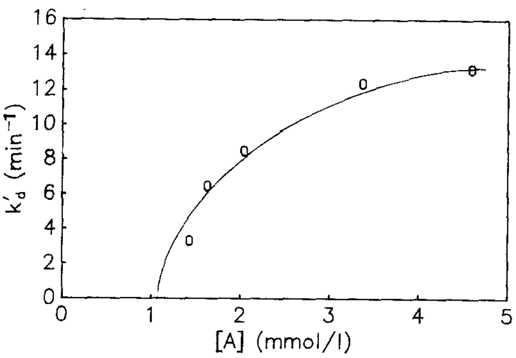


FIG. 10. Plot of decay rate constants vs different amounts of Al(i-Bu)$_3$. Polymerization conditions: P_E = 166.7 psia, T = 70°C.

Effect of Monomer Concentration on the Deactivation

There is no effect of the monomer concentration on the decay rate of the polymerization, as shown in Fig. 12. From the slopes in Fig. 12, k_d' can be calculated to be 8.5 min^{-1} regardless of monomer pressure. This result indicates that the deactivation process is not involved with diffusion through the polymer. However, the dependence of monomer concentration on deactivation was reported for the polymerization of propylene in Ziegler–Natta catalysis (*23*, *24*).

Effect of Temperature on the Deactivation

Figure 7 shows that the decay rate of polymerization becomes faster at higher temperature. From the Arrhenius plot in Fig. 13, the activation energy of k_d' ($E_{k,d}$), 15.8 kcal/mol, could be obtained.

Effect of Temperature on the Maximum Rate of Polymerization

If the concentration of active polymerization centers reaches its maximum value, $[C^*]_{max}$, after the period of active center formation, the maximum rate of polymerization, $R_{p,max}$, can be expressed as

$$R_{p,max} = k_p \theta_M [C^*]_{max}. \qquad (17)$$

Table 6 shows the maximum rate of polymerization and its corresponding time (t_{max}) in the temperature range between 323 and 353 K. As shown in Table 6, t_{max} becomes shorter at higher temperature, which indicates that the active polymerization center is more rapidly formed at higher temperature. As shown in Fig. 14, the Arrhenius plot of $R_{p,max}$, negative activation energy appears above 343 K. Many authors reported the observation of negative activation energy at high temperature in Ziegler–Natta catalysis (*25*) and in CrO$_3$/SiO$_2$ catalysis (*26*). The reason for the appearance of negative activation energy of the maximum polymerization rate might be diffusion limitation due to swelling in a slurry polymerization system. However, from the fact that decay rate constants are the same value regardless of monomer concentra-

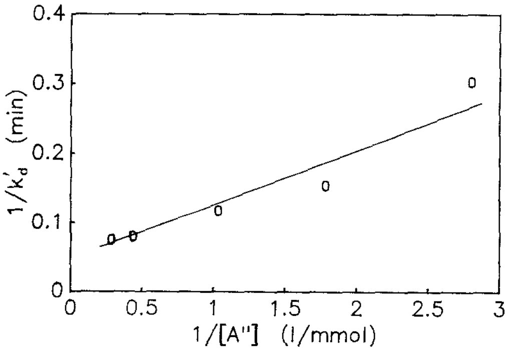


FIG. 11. Linear plot of $1/k_d'$ vs $1/[A'']$, by Eq. (14). Same polymerization conditions as those in Fig. 9.

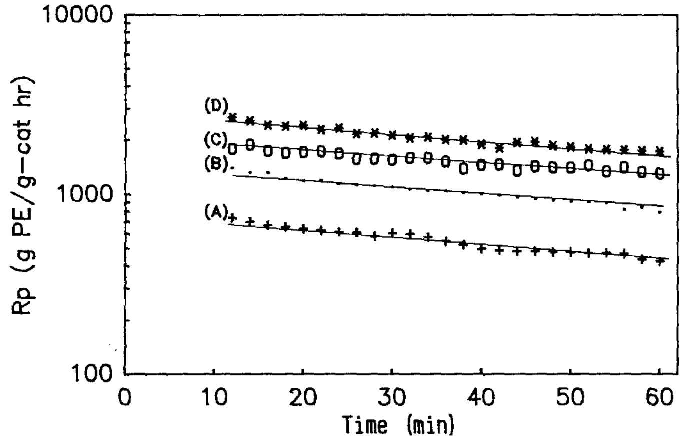


FIG. 12. Logarithmic plot of polymerization rate vs various monomer pressures. Temperature = 70°C, [A] = 2.04 mmol/liter. P_E in psia: (A) 116.7, (B) 166.7, (C) 218.7, (D) 268.7.

tion, it is more reasonable that the active site undergoes chemical change, deactivation. Below 343 K, the activation energy of the maximum rate of polymerization ($E_{p,max}$), 8.8 kcal/mol, could be obtained. This value is compared with the activation energy of the steady-state polymerization rate, 10 kcal/mol, in the CrO_3/SiO_2 catalyst system (*26*). From the value of $E_{p,i}$, 9.8 kcal/mol, determined previously and the following relationship for $E_{k,1}$, the activation energy of active center formation is Eq. (1).

$$E_{k,1} = E_{p,i} - E_{p,max}, \qquad (18)$$

$E_{k,1}$, 1.0 kcal/mol, can be obtained. This value is very small compared with $E_{k,d}$, 15.8 kcal/mol, which shows that the deactivation process is much more sensitive to temperature than the activation process.

CONCLUSION

Kinetic study was carried out to investigate the effect of Al(i-Bu)$_3$ on CrO_3/SiO_2 catalyst. The interaction of Al(i-Bu)$_3$ with preactive sites can be interpreted by a simple model which shows that adsorbed Al(i-Bu)$_3$ reduces and alkylates the preactive sites to make active polymerization sites. The rate of propagation can be expressed by the product of adsorbed ethylene and active sites. Deactivation, which is not de-

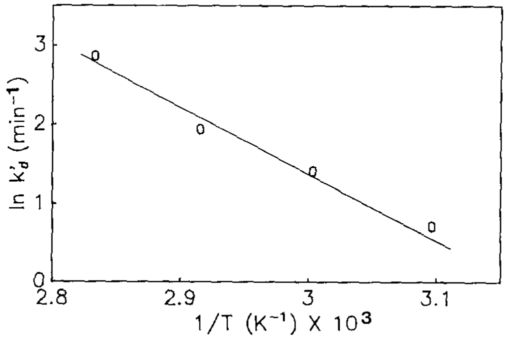


FIG. 13. Arrhenius plot of decay rate constants.

TABLE 6

Maximum Rates of Polymerization and Corresponding Times with Various Temperatures (Polymerization Conditions: [A] = 2.04 mmol/liter, [M] = 1.1786 mmol/liter)

Temp(K)	$R_{p,max}$(g PE/g cat. hr)	t_{max} (min)
323	776	15
333	1095	14
343	1734	11
353	1407	3

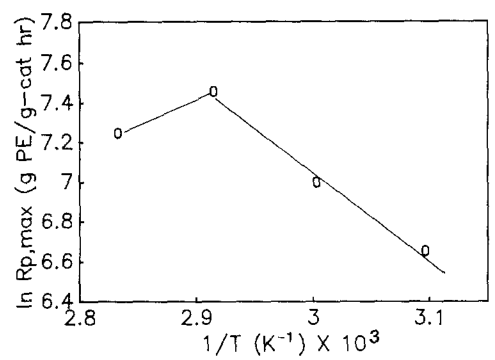


FIG. 14. Arrhenius plot of maximum polymerization rate.

pendent on monomer pressure, begins when excess Al(i-Bu)$_3$ is added. This phenomenon can be interpreted as the deactivation of the active sites by adsorbed Al(i-Bu)$_3$. The reason for deactivation might be due to the over-reduction, Cr^{2+} to Cr^{1+}, or to Cr^0. It can be concluded that the number of active polymerization centers, which is dependent on temperature and concentration of Al(i-Bu)$_3$, is changing during polymerization time. However, it cannot be excluded that k_p values may change during the polymerization because of site modification by Al(i-Bu)$_3$. From the former point of view, the negative activation energy of the propagation rate constant can be interpreted by the decrease in the number of active centers from the fact that the destruction rate of active sites is faster than the rate of formation at higher temperature.

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