

# Polymerization of Propylene Using a Prepolymerized High-Active Ziegler–Natta Catalyst. I. Kinetic Studies

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## SYNOPSIS

The kinetics of propylene polymerization using a prepolymerized high-active  $\text{TiCl}_3$  catalyst with an  $\text{Et}_2\text{AlCl}$  cocatalyst are investigated. The effect of various parameters such as Al/Ti ratio, pressure, temperature, hydrogen, and polymerization time on the rate of polymerization and yield are examined. The dependency of these parameters on the polymerization rate are studied. It is found that the variation at the rate of polymerization with the  $\text{Et}_2\text{AlCl}$  cocatalyst concentration complies with a Langmuir–Hinshelwood type of relationship. The overall activation energy of polymerization calculated from the Arrhenius plot was found to be 11.6 kcal/mol. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The polymerization of propylene in a heptane diluent over heterogeneous Ziegler–Natta catalysts has been the subject of extensive research and numerous catalyst systems have been investigated for the polymerization of propylene.<sup>1–10</sup> Not only the activity and selectivity but also the morphology of the Ziegler–Natta catalysts is an important parameter in the polymerization of propylene. To better control the polymerization conditions and product properties, prepolymerization techniques were developed which are often used to control the morphology of the catalyst grains by conducting a controlled polymerization stage to maintain controlled initial particle growth. The effect of various conditions on prepolymerization were investigated and both average propylene polymerization rate and bulk density increased by prepolymerized catalysts.<sup>11,12</sup> In this work, the effect of polymerization parameters on the kinetics and the particle morphology were investigated using prepolymerized high-active  $\text{TiCl}_3$  catalysts which are approximately 10 times as active as are classical first-generation  $\text{TiCl}_3$  catalysts. The objective of this first article was to show the effect of the

aluminum/titanium (Al/Ti) ratio, pressure and, thus, monomer concentration, temperature, hydrogen concentration, and duration of polymerization on the polymerization rate. In the second part, the effect of polymerization parameters on the product properties and polymer morphology will be given.

## EXPERIMENTAL

### Materials

#### *Propylene*

Polymerization-grade propylene with a minimum purity of 99.95 (vol %) was obtained from PETKİM Petrochemicals Inc. The monomer was dried over molecular sieves (3 Å).

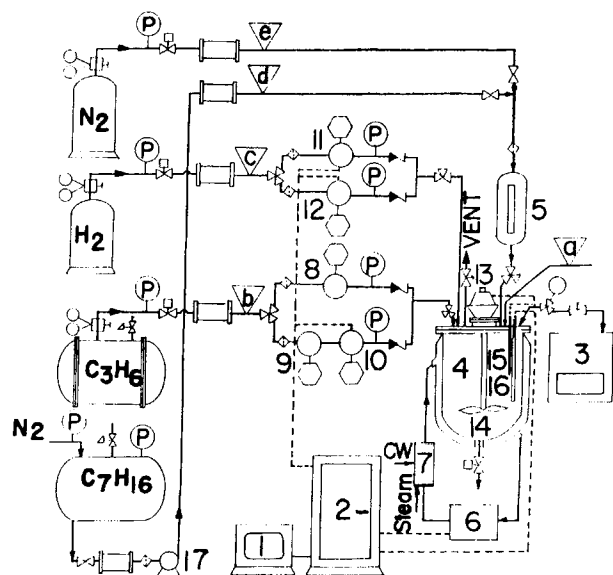
#### *n-Heptane*

*n*-Heptane with a minimum purity of 90 wt %, which is in the boiling range of 60–70°C, was obtained from PETKİM Petrochemicals Inc. The solvent was passed through molecular sieves (13×).

#### *Diethyl Aluminum Chloride (DEAC)*

DEAC was supplied by Texas Alkyls Inc. and was used at 20 wt % in heptane. The Cl/Al mol ratio of DEAC = 1.01.

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**Figure 1** Polymerization system: (1) IBM computer; (2) interface unit; (3) gas chromatography; (4) polymerization reactor; (5) *n*-heptane transfer tank; (6) thermostat; (7) heat exchanger; (8)  $C_3H_6$ -mass flow controller and totalizer; (9)  $C_3H_6$ -mass flowmeter with totalizer; (10)  $C_3H_6$ -pressure controller; (11)  $H_2$ -high-level mass flow controller; (12)  $H_2$ -low-level mass flow controller; (13) variable-speed agitator; (14) impeller; (15) thermocouple; (16) pressure transducer; (17) pump.

### Prepolymerized Titanium Catalyst

A prepolymerized high-active titanium catalyst was obtained from Catalyst Resources Inc.

### Hydrogen and Nitrogen

Ultrahigh purity hydrogen and nitrogen were obtained from BOC Ltd. and were used without further purification.

### Polymerization

Polymerizations were carried out with the polymerization system shown in Figure 1. The catalyst components were prepared in a glove box where the moisture and oxygen was measured and kept below 10 ppm. The gas feedstocks were kept in pressurized cylinders and sent to the reactor passing through 3 Å molecular sieve beds and/or oxygen scavengers to keep moisture and oxygen below 2–4 ppm. Rates and quantities of hydrogen and propylene fed to the reactor were measured and controlled by mass flow meters and controllers. The solvent, *n*-heptane, was pumped over a bed of 3 Å molecular sieves to keep its water content below 5 ppm. The catalyst com-

ponents were transferred to the reactor using special containers.

The temperature of the reactor was controlled within a  $\pm 0.5^\circ\text{C}$  deviation by suitable temperature controllers. The pressure of the reactor was controlled by pressure controllers. The reactor was provided with specially designed agitators for uniform mixing of the solids. The agitator speed was adjustable between 0 and 2000 rpm using a special magnetic drive motor. The composition of the gas phase in the reactor was continuously monitored by on-line gas chromatography (GC). The temperature, pressure, feed rates, and sampling for GC analysis were controlled by a microprocessor and its relevant interface unit.

Polymerizations were carried out with the recipe shown in Table I. The reactor was heated to  $120^\circ\text{C}$  and an approximate  $10^{-3}$  mmHg vacuum was applied for 12 h to remove any trace impurities adsorbed on reactor internal surfaces. After this passivation step, the reactor was purged three times with propylene; then, the temperature was set to  $65^\circ\text{C}$  and *n*-heptane and propylene were fed to adjust the pressure of the reactor to  $0.5 \text{ kg/cm}^2 \text{ G}$ . The agitation speed was adjusted to 200 rpm and the DEAC solution in *n*-heptane, which was prepared in the glove box, was transferred to the reactor with a special container. Then, the prepolymerized titanium catalyst previously prepared in the glove box and put into a special container was transferred into the reactor. After the catalyst addition, the reactor was closed, agitator speed was increased to 800 rpm, the required amount of hydrogen was fed, and heating of the reactor was started together with continuous feeding of propylene to keep the pressure of the reactor at  $3 \text{ kg/cm}^2 \text{ G}$ . The heating rate was adjusted so that the reactor reached  $70^\circ\text{C}$  in 5 min after the catalyst addition. After the temperature reached to  $70^\circ\text{C}$ , the pressure

**Table I** Propylene Polymerization Recipe

Chemical	Quantity
<i>n</i> -Heptane	2500 mL
DEAC	2.62 g
Catalyst	0.27 g
Hydrogen	1000 N mL
Propylene	Amount consumed at $6 \text{ kg/cm}^2 \text{ G}$ constant pressure
Temperature	$70^\circ\text{C}$
Pressure	$6 \text{ kg/cm}^2$
Time	2 h
Al/Ti	6.4 mol/mol

**Table II** Influence of Catalyst Concentration on Yield and Polymer Rate

Amount of TiCl <sub>3</sub> (mol)	TiCl <sub>3</sub> Concn (mol/L)	Yield (g PP/g TiCat)	Average Rate (g PP/g TiCat h)
$8.75 \times 10^{-4}$	$3.50 \times 10^{-4}$	1499	750
$1.75 \times 10^{-3}$	$7.00 \times 10^{-4}$	1556	778
$2.92 \times 10^{-3}$	$1.17 \times 10^{-3}$	1401	700

of the reactor was adjusted to 6 kg/cm<sup>2</sup> G by feeding propylene.

Propylene feeding under these conditions was continued for 2 h. Then, the unreacted monomer was vented and the polymer slurry was deactivated by adding butanol. The temperature was kept at 70°C during the catalyst deactivation and the slurry was agitated for 30 min. Then, the slurry was filtered and washed with heptane. The filtered wet cake was dried in a vacuum oven at 50°C, 760 mmHg vacuum, for approximately 3 h. The solution obtained from filtration was kept for atactic polypropylene (APP) content determination. During the polymerization, the consumptions of propylene and hydrogen were followed by a flow totalizer and by an on-line gas chromatography, respectively.

#### Test Methods and Analytical Produces

The quality of monomers, catalysts, and the other chemicals were checked in line with relevant test methods.<sup>13</sup>

## RESULTS AND DISCUSSION

The main aim of this work was to investigate the kinetic behavior of prepolymerized high-active titanium catalyst. To investigate the effects of various parameters on the polymerization rate, polymerizations were carried out by changing the tested parameter while keeping the others constant. The investigated parameters were the aluminum/titanium

ratio, pressure and, thus, monomer concentration, temperature, hydrogen concentration, and duration of polymerization.

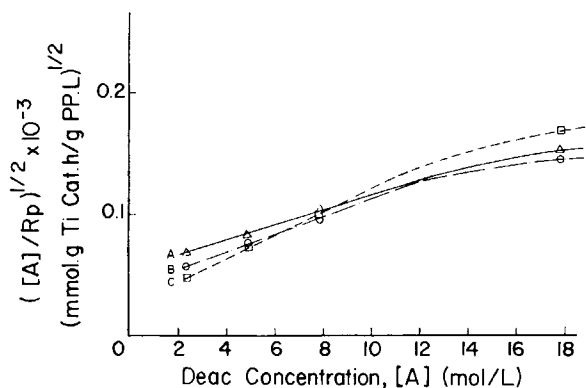
#### Elimination of the Effect of Mass Transfer Resistance

##### External Mass Transfer Resistance

To eliminate the effect of external mass transfer resistance, the polymerization rate must be kept at less than the rate of transport of gaseous propylene to the polymerization slurry. To determine whether an external mass transfer resistance is present during polymerization, polymerization rates are measured by changing the stirring speed and the amount of the catalyst used. Above 200 rpm, the polymerization rate does not change at a catalyst concentration of  $7.0 \times 10^{-4}$  mol/L. This result shows that there is no external mass transfer resistance at this concentration when agitation speeds are kept higher than 200 rpm. As seen from Table II, above 200 rpm, the polymerization rate is linearly proportional to the amount of catalyst when the concentration of the catalyst is less than  $1.17 \times 10^{-3}$  mol/L. Therefore, it can be concluded that there is no external mass transfer resistance at the investigated catalyst concentrations provided that the agitation speed is kept above 200 rpm. The catalyst concentration of  $7 \times 10^{-4}$  mol/L and agitation speed of 800 rpm are used throughout the study; the other parameters are kept constant as shown in Table I.

**Table III** Influence of Al/Ti Ratio on Yield and Polymer Rate

Al/Ti (mol/mol)	Aluminum Concn (mol/L)	Yield (g PP/g TiCat)	Average Rate (g PP/g TiCat h)
3.6	$2.5 \times 10^{-3}$	1498	749
7.2	$5.0 \times 10^{-3}$	1578	789
11.5	$8.0 \times 10^{-3}$	1567	784
25.9	$18.0 \times 10^{-3}$	1419	710



**Figure 2** Langmuir-Hinshelwood plot. Polymerization time: (A) 60 min; (B) 20 min; (C) 120 min.

### Internal Mass Transfer Resistance

The Thiele modulus,  $\alpha$ , which is the ratio of the characteristic diffusion time to the characteristic reaction time, is given by

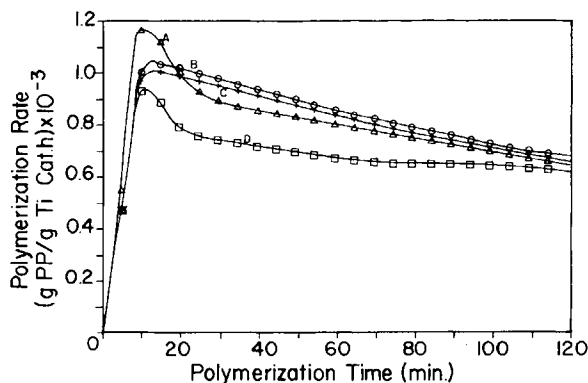
$$\alpha = \left( \frac{K_p C_0^*}{Dm} \right)^{1/2} S_0$$

where  $k_p$  = the propagation rate constant ( $\text{mol-site}^{-1} \text{s}^{-1}$ ),  $C_0^*$  = the initial concentration of the active center,  $Dm$  = the diffusivity of propylene ( $\text{cm}^2 \text{s}^{-1}$ ), and  $S_0$  = the initial radius of catalyst particle.<sup>15</sup>

Since the rate of polymerization is

$$R_p = k_p [C^*] [m]_p$$

where  $[m]_p$  is the monomer concentration in the polymer, the Thiele modulus could be given as



**Figure 3** Effect of DEAC concentration on polymerization rate. Polymerization conditions:  $T = 70^\circ\text{C}$ ; catalyst weight = 0.27 g; pressure = 6  $\text{kg/cm}^2 \text{G}$ ; hydrogen quantity 1000 N mL; DEAC concentration: (A) 2.5; (B) 5.0; (C) 8.0; (D) 18.0 mmol/L.

**Table IV** Influence of Polymerization Pressure on Yield and Polymer Rate

Pressure (kg/cm <sup>2</sup> G)	Yield (g PP/g TiCat)	Initial Rate (g PP/g TiCat h)
4.0	1221	1200
6.0	1595	1500
9.0	2611	1950
12.0	3462	2400

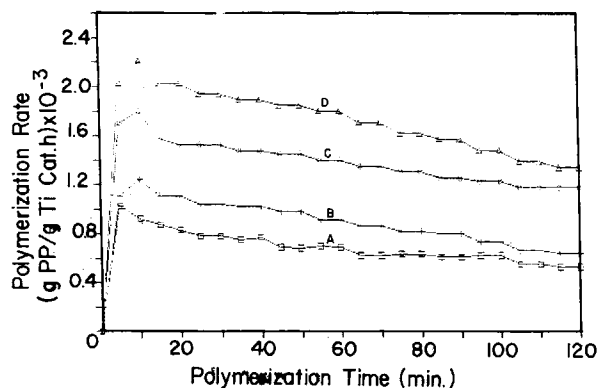
$$\alpha = \left( \frac{R_p}{Dm[m]_p} \right)^{1/2} S_0$$

and can be used to estimate the degree of diffusion control; a large value of  $\alpha$  ( $>10$ ) indicates the presence of a diffusion limitation, while a small value of  $\alpha$  less than 1 indicates the absence of a diffusion limitation.

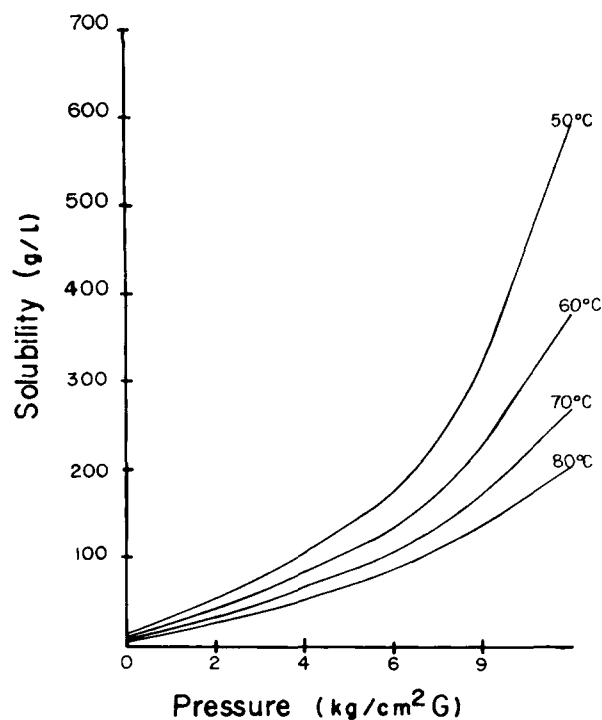
By using  $Dm = 6.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  and  $S_0 = 1 \times 10^{-4} \text{ cm}$ , we obtained a value of  $\approx 3.5 \times 10^{-2}$  for  $R_p = 1306 \text{ gPP/gTiCat h}$ , which is the highest polymerization rate observed during the trials. This value of  $\alpha$  is very small, indicating that there is no internal mass transfer resistance in this catalytic system. As a result, it is concluded that external or internal mass transfer resistances are not involved in our polymerization reaction conditions.

### Effect of Aluminum Cocatalyst Concentration on Polymerization Rate

The composition of the catalyst system represented by the Al/Ti molar ratio is an important reaction

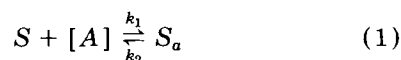


**Figure 4** Effect of monomer pressures on polymerization rate. Polymerization conditions:  $T = 70^\circ\text{C}$ ; catalyst weight = 0.27 g; DEAC = 4.4 mmol/L; hydrogen quantity 1000 N mL; pressures: (A) 4; (B) 6; (C) 9; (D) 12  $\text{kg/cm}^2 \text{G}$ .



**Figure 5** Solubility of propylene in *n*-heptane (calculated by Hysim process simulation software).

parameter in the polymerization of propylene. The variation of the Al/Ti ratio was investigated by keeping the amount of  $\text{TiCl}_3$  constant and varying the amount of DEAC. Table III shows the influence of Al/Ti ratio on polymerization. The order of addition of DEAC also affects the kinetic behavior of polymerization. In this study, DEAC is introduced into the reactor containing heptane; then, the catalyst and monomer is fed simultaneously to the reactor. When DEAC and the monomer contacts the catalyst active sites, a competitive adsorption takes place and active sites form as shown below:



where  $S$  stands for catalyst surface site,  $[A]$  for the concentration of DEAC,  $[M]$  for the concentration of the monomer, and  $S_a$  for the active sites.

Then, the reaction takes place forming polymerization centers,  $C_p$ :



where  $k_1$ ,  $k_2$ ,  $k_3$ ,  $k_4$ ,  $k_5$ , and  $k_6$  are the relevant rate constants. The reaction at the polymerization sites could be approximated as follows:

$$\frac{dC_p}{dt} = k_5[S_a][A] + k_6[S_a][M] \quad (5)$$

$$\frac{dC_p}{dt} = \left(k_5 + k_6 \frac{K_A}{K}\right)[S_a][A] \quad (6)$$

where  $K_A$  and  $K$  are adsorption equilibrium constants for DEAC and the monomer, respectively.

The total sites at the beginning of polymerization  $[S_a]_0$  is equal to sites occupied by DEAC, the monomer, and polymer molecules:

$$[S_a]_0 = [S_a] + [C_p] \quad (7)$$

By substituting eq. (7) and solving eq. (6), one gets

$$C_p = [S_a]_0[1 - \exp(-k_5 + k_6 K_A/K_M)[A]t)] \quad (8)$$

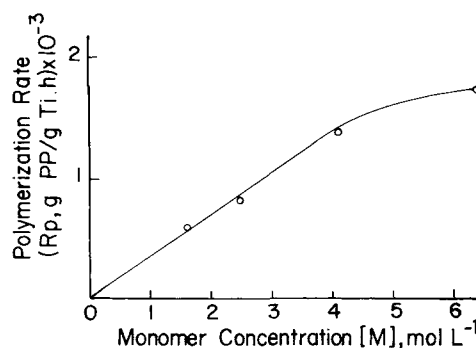
The rate of polymerization could be expressed by the following equation:

$$R_p = k_p(k_5 + k_6 K_A/K_M)[M][A][S_a]_0 t \quad (9)$$

Equation (9) could be simplified by substituting  $K = k_p(k_5 + k_6 K_A/K)[S_a]_0$ :

$$R_p = K[M][A]t \quad (10)$$

Equation (10) denotes that the rate of polymerization is directly proportional to concentration of DEAC and the monomer.



**Figure 6** Dependence of the polymerization rate on the monomer concentration. Polymerization conditions:  $T = 70^\circ\text{C}$ ; catalyst weight = 0.27 g; DEAC = 4.4 mmol/L; hydrogen quantity = 1000 N mL.

**Table V Influence of Polymerization Temperature on Yield and Polymer Rate**

Temperature (°C)	Monomer Concn (mol/L)	Yield (g PP/g TiCat)	Initial Rate (g PP/g TiCat h)
60	2.25	904	1030
70	1.95	1434	1230
80	1.70	1890	1300
90	1.50	1330	1700

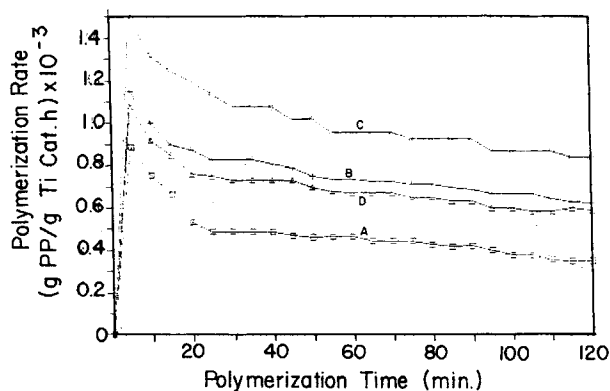
In the polymerization of propylene on a heterogeneous catalyst surface, not only the reactants DEAC and the monomer, but also the product is absorbed on the catalyst surface; this implies that a Langmuir-Hinshelwood type of kinetics could be applied. This mechanism could be represented by the following equation:

$$R_p = \frac{kK_M K_A [A][M]}{(1 + K_A [A] + K_M [M])^2} \quad (11)$$

If the adsorption equilibrium rate constant of DEAC is much greater than that of the monomer, eq. (11) could be arranged as follows:

$$R_p = k' \frac{K_A [A]}{(1 + K_A [A])^2} \quad (12)$$

To check if the data fit the proposed mechanism, the influence of the mol ratio of cocatalyst to catalyst was investigated at a constant monomer concentration by the Langmuir-Hinshelwood plot, as shown



**Figure 7** Dependence of the polymerization rate on the polymerization temperature. Polymerization conditions: pressure = 6 kg/cm<sup>2</sup> G; catalyst weight = 0.27 g; DEAC = 4.4 mmol/L; hydrogen quantity 1000 N mL; temperatures: (A) 60°C; (B) 70°C; (C) 80°C; (D) 90°C.

in Figure 2, which is the plot of  $(A/R_p)^{1/2}$  vs. concentration of DEAC at various polymerization times. Linear plots are obtained for different polymerization times in the Al/Ti mol ratio range of 3–11.5.

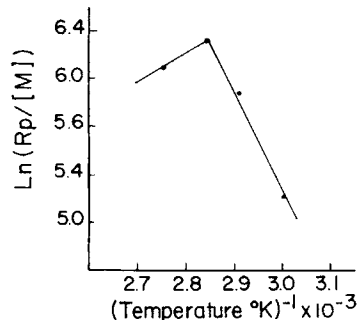
Therefore, it is concluded that the Langmuir-Hinshelwood type of kinetics is valid for the investigated catalyst system and the activation of titanium sites by DEAC is the rate-determining step for the formation of polymerization centers during the initial period of polymerization.

Figure 3 shows the polymerization rate curves at various concentrations of DEAC. As the concentration of DEAC increases, the time to reach a maximum rate first increases, then above a concentration of  $5.0 \times 10^{-3}$  mol/L the rate starts to decrease. Using the data of Figure 2, the value of  $K$  is calculated from eq. (10) as  $6.4 \times 10^{-3}$  g C<sub>3</sub>H<sub>6</sub> L/g TiCat h.

The decrease in the rate at high Al/Ti ratios could be attributed to the competitive adsorption between DEAC and monomer on the same site or the formation of less active species such as ethylaluminum dichloride (EADC).<sup>14</sup>

### Effect of Monomer Concentration

The rate of polymerization is usually expressed by the following equation:



**Figure 8** Arrhenius plot of the average overall polymerization rate. Polymerization conditions are the same as those in Figure 7.

**Table VI** Reported Activation Energies in Propylene Polymerization

Workers	Catalyst System	$E_a$ (kcal/mol)
Natta et al. <sup>16</sup>	—TiCl <sub>3</sub> /TEA	10
Keii et al. <sup>17-19</sup>	TiCl <sub>3</sub> /DEAC	13.5
Grigorev et al. <sup>20</sup>	TiCl <sub>3</sub> /TEA	11.5–12.5
Yuan et al. <sup>10</sup>	TiCl <sub>3</sub> · 1/3AlCl <sub>3</sub> /DEAC	11.2
Kahraman et al. <sup>13</sup>	TiCl <sub>3</sub> · 1/3AlCl <sub>3</sub> /DEAC	11.6
This work	Prepolymerized TiCat	11.9

$$R_p = K[C][M]$$

where  $R_p$  is the rate of polymerization;  $K$ , the rate constant of propagation;  $[C]$ , the concentration of active sites; and  $[M]$ , the concentration of propylene in heptane.

The effect of monomer concentration was investigated by conducting polymerizations at four different pressures: 4, 6, 9, and 12 kg/cm<sup>2</sup> G. The results obtained are shown in Table IV and Figure 4.

The concentration of the monomer was calculated by the Hysim Ver. 2.10. Process Simulation Software based on UNIQUAC and Peng Robinson equations. As seen from Figure 5, the solubility of propylene gas increases with increasing propylene pressure; the polymerization rates for different monomer concentrations are shown in Figure 6. It was found that the rate of polymerization is of first order with respect to the monomer concentration up to a monomer concentration of 4 mol/L, and above this concentration, the rate of polymerization deviates from linearity.

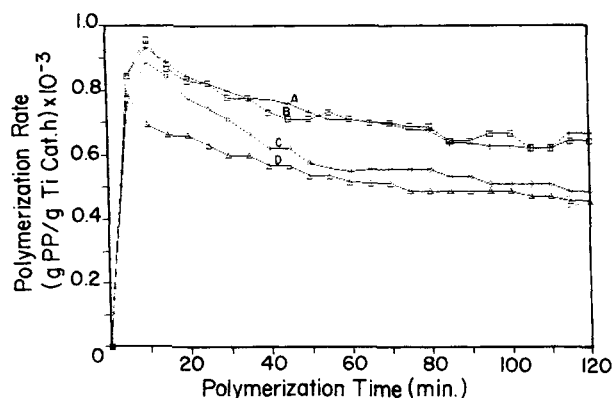
### Effect of Polymerization Temperature

The effect of polymerization temperature was investigated between 60 and 90°C and the results obtained are shown in Table V. The dependencies of polymerization rates on polymerization temperatures is shown in Figure 7. The polymerization rate

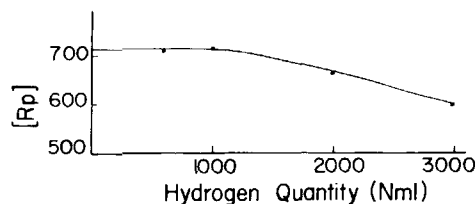
rapidly declines during the early stages of polymerization; thus, the rate is somewhat dependent on the duration of the experiment. The rates of polymerizations are calculated on the basis of 2 h. The rate of polymerization increases as temperature increases. As seen from Table V, the yield and therefore the polymerization rate increases as temperature increases. But at temperatures above 80°C, the polymerization rate decreases. An Arrhenius plot prepared by the data given in Table V is shown in Figure 8. The apparent activation energy calculated from the average rate over 2 h at 60–80°C is 11.9 kcal/mol. The estimated value is found to be in general agreement with several other workers, as shown in Table VI.<sup>13-20</sup> As seen from Figure 8, there is an apparent break in the curve over 80°C, which was also obtained by Choi and Ray.<sup>21</sup> The apparent activation energy calculated from the average rate over 2 h at 80–90°C is -5.7 kcal/mol. The phenomenon was attributed to the deactivation of active sites at high temperatures.<sup>22</sup> It is postulated that the observed rate differences can be explained through the sorption theory.<sup>23</sup> The rate of reaction is propor-

**Table VII** Influence of Partial Pressure of Hydrogen on Yield and Polymer Rate

Hydrogen Feed (N mL)	Yield (g PP/g TiCat)	Average Rate (g PP/g TiCat h)
600	1423	711
1000	1434	717
2000	1325	662
3000	1200	600



**Figure 9** Effect of hydrogen partial pressures on the polymerization rate. Polymerization conditions:  $T = 80^\circ\text{C}$ ; pressure = 6 kg/cm<sup>2</sup> G; catalyst weight = 0.27 g; DEAC = 4.4 mmol/L; hydrogen quantity: (A) 600; (B) 1000; (C) 2000; (D) 3000 N mL.



**Figure 10** Effect of hydrogen on the average polymerization rate. Polymerization conditions are the same as those in Figure 9.

tional to monomer concentration sorped by the amorphous regions of the polymer. The monomer concentration in amorphous polymer decreases by temperature and, consequently, the reaction rate decreases.

### Effect of Hydrogen

Hydrogen is a very efficient chain-transfer agent for the polymerization of propylene. Hydrogen consumption depends on the characteristics of the catalyst and the amount of reactive impurities in the raw materials. The effect of hydrogen is investigated at four hydrogen levels, keeping the total pressure of polymerization constant. The results are presented in Table VII and Figure 9.

As shown in Figure 10, the rate of polymerization does not change up to 1000 N mL of hydrogen quantity; then, the rate decreases, as a result of decreasing effective monomer concentration near catalytically active sites due to adsorbed hydrogen.

### Effect of Polymerization Time

The polymerization rate decreases by the time in the slurry polymerization of propylene. Each catalyst system has its own characteristic rate decay profile. The rate decay profile is a very important parameter for the optimization of reactor productivity and thus has economic importance. The rate decay behavior of the catalyst system is investigated by elongating the time of polymerization to 6 h. The results obtained are shown in Table VIII and Figure 11. When rate data are examined, it can be seen that an apparently continuous rate decline is observed.

The data were examined on generalized equation for the decay of catalytic reaction with time:

$$\frac{d_r}{d_t} = -k_d r^n$$

**Table VIII** The Variation of Yield and Polymer Rate with Polymerization Time

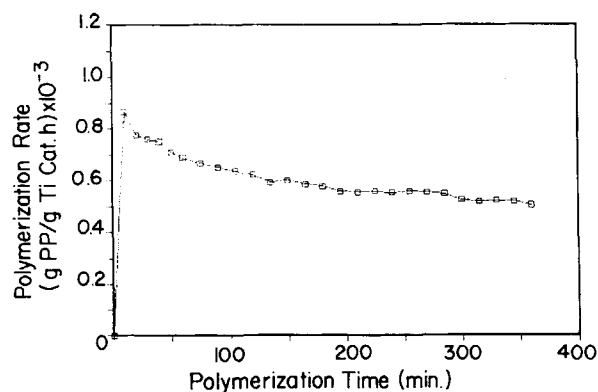
Time (h)	Yield (g PP/g TiCat)	Average Rate (g PP/g TiCat h)
1	815	815
2	1567	784
6	3233	539

where the exponent,  $n$ , which is the order of the decay process. First-, 1.5-, and second-order decay models were investigated. The percentage discrepancies for each model is shown on Table IX. The measurement of propylene consumption could be subject to experimental uncertainty at the early stages of these very rapidly decaying polymerizations. Therefore, the yield values are used after 1 h for the evaluation. The investigation also showed that the second model seems to be the most accurate correlation for the polymerization times from 0 to 2 h.

### CONCLUSION

Propylene polymerizations were performed using a prepolymerized high-active Ziegler-Natta catalyst with DEAC as a cocatalyst to investigate the effect of polymerization parameters on the polymerization rate.

From the kinetic studies, the following results were obtained within investigated polymerization limits:



**Figure 11** Dependence of the polymerization rate on the polymerization time. Polymerization conditions:  $T = 80^\circ\text{C}$ ; pressure = 6 kg/cm<sup>2</sup> G; catalyst weight = 0.27 g; DEAC = 4.4 mmol/L; hydrogen quantity 1000 N mL.



Table IX Percentage Discrepancies For Rate Decay Kinetic Models

Time (Min)	Data Base on C <sub>3</sub> Consumption			Date Base on Yield		
	First Order	1.5 Order	Second Order	First Order	1.5 Order	Second Order
0	0	0	0			
30	-2.2	-0.7	0			
60	-4.8	+2.4	+1.6	%2	8	1.3
90	+5.2	-2.6	-1.7	%0	11.4	-1.4
120	+5.6	-2.8	-1.9			
150	-4.9	-2.0	-0.9			
180	-4.1	-2.1	0.0			
210	-2.2	-1.1	0.0			
240	+1.1	0	2.2			
270	+2.4	1.2	2.4			
300	-5.4	9.5	-6.8			
330	+7.5	2.5	3.8			
360	+9.3	+1.3	+2.6	13	57	33.5

% Error = (actual data - calculated data)/actual data × 100.

1. Polymerization rate profiles are dependent on the polymerization condition of aluminum cocatalyst concentration, pressure and, thus, monomer concentration, temperature, hydrogen concentration in gas phase, and polymerization time.
2. When the aluminum cocatalyst concentration increases, the rate of polymerization increases; then for a certain range of concentration, the rate of polymerization does not change.
3. The variation of the rate of polymerization with an aluminum cocatalyst concentration is consistent with a Langmuir-Hinshelwood type of relationship.
4. The rate of polymerization is a first-order reaction with respect to monomer concentration up to 4 mol/L, and above this concentration, the rate of polymerization decreases.
5. The rate of polymerization increases up to 80°C but it decreases above 80°C because of the decrease of monomer concentration in the polymer phase.
6. The apparent activation energy for the overall rate of polymerization is 11.9 kcal/mol between 60 and 80°C.
7. The rate of polymerization decreases at high hydrogen concentration, because adsorbed hydrogen lowers the effective monomer concentration near catalytically active sites.
8. The rate of polymerization slightly decreases

in time, and the second-order decay equation is in good correlation between 0 and 2 h.

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