Propylene Polymerization in Slurry Catalyzed by Titanium Trichloride–Diethyl Aluminum Chloride

R. KAHRAMAN, M. ERDOĞAN, T. BILGIÇ,* and Ö. T. SAVAŞÇI

Petkim Petrochemicals Holding Inc., Research & Development Centre, P.K. 46, 41001 İzmit, Turkey

SYNOPSIS

Propylene is polymerized in a slurry over a $TiCl_3 \cdot \frac{1}{3} AlCl_3$ catalyst with a DEAC cocatalyst, approaching conditions of industrial relevance. The effects of various parameters such as temperature, pressure, cocatalyst-to-catalyst ratio, hydrogen concentration, and polymerization time are investigated with particular emphasis on the yield, tacticity, molecular weight, bulk density, and particle size of the resulting polymer. The highest yield and isotactic content are obtained at an Al/Ti ratio of 6, temperature of 70°C, and pressure of 9 kg/cm² g. The polymerization rate is found to be first order up to a monomer concentration of 2.5 mol/L. The overall activation energy of polymerization calculated from an Arrhenius plot is found to be 11.6 kcal/mol. A correlation between MFI and molecular weight is also presented. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The polymerization of propylene over heterogeneous Ziegler–Natta catalysts has been the subject of extensive research and attempts have been made to understand its kinetics. Numerous catalyst systems have been investigated for the polymerization of propylene[1-7] including the $TiCl_3 — (C_2H_5)_2AlCl$ system, which is one of the oldest commercial ones. However, as in the previous work of Chien[8] and Yuan et al.,[9] in the information made available in the literature, the investigated number of parameters are limited and their ranges do not approach those of the industrial applications. Therefore, in this work, an attempt has been made to investigate the catalyst system in question under conditions of industrial relevance covering broad ranges of temperatures, pressures, cocatalyst-to-catalyst ratios, and hydrogen concentrations including change of catalyst activity and selectivity by time. Average particle sizes, bulk densities, and molecular weights of the polymers produced are also investigated.

EXPERIMENTAL

Materials

Polymerization-grade propylene with a minimum purity of 99.95%; n-heptane, 90% of which is in the boiling range of 60–70°C; and a first-generation $TiCl_3 \cdot \frac{1}{3} AlCl_3$ catalyst were used, all of which were obtained from PETKİM Petrochemicals as commercial products. Ultrahigh-purity nitrogen and hydrogen were obtained from BOC (UK) and the cocatalyst, diethylaluminum chloride (DEAC), was supplied by Texas Alkyls (USA).

Polymerization

Polymerizations were carried out with the polymerization system shown in Figure 1. The catalyst components are prepared in a glove box where the moisture and oxygen is measured and kept below 10 ppm. The gas feedstocks are kept in pressurized cylinders and sent to the reactor passing through 3 Å molecular sieve beds and/or oxygen scavengers to keep the moisture and oxygen below 2–4 ppm. Rates and quantities of hydrogen and propylene fed to the reactor are measured and controlled by mass flowmeters and controllers. The solvent, n-heptane, is
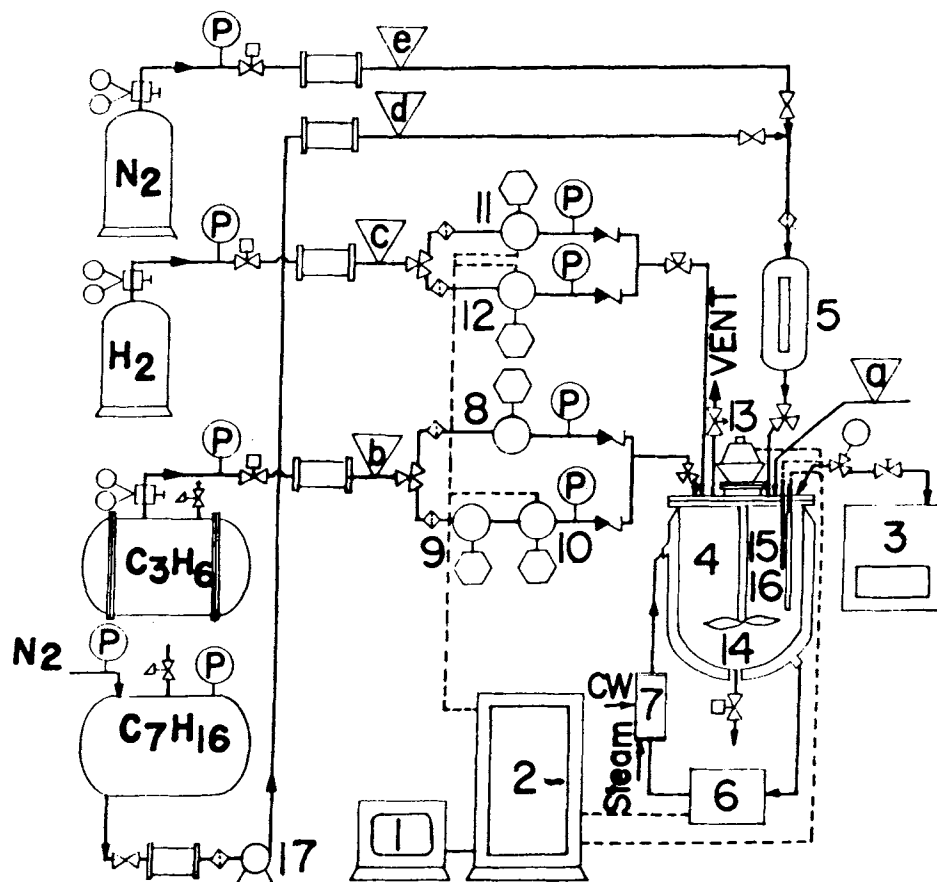
Figure 1 Polymerization system: (1) IBM computer; (2) Interface unit; (3) gas chromatography; (4) polymerization reactor; (5) n-heptane transfer tank; (6) thermostat; (7) heat exchanger; (8) C_3H_6-mass flow controller and totalizer; (9) C_3H_6-mass flowmeter with totalizer; (10) C_3H_6-pressure controller; (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.

pumped over a bed of 3 Å molecular sieve to keep its water content below 5 ppm. The catalyst components are transferred to the reactor by means of special containers.

The temperature of the reactor is controlled within a ±0.5°C deviation by suitable temperature controllers. The pressure of the reactor is controlled by pressure controllers. The reactor is provided with specially designed agitators for uniform mixing of the solids. The agitator speed is adjustable between 0 and 2000 rpm using a special magnetic drive motor. The composition of the gas phase in the reactor is continuously monitored by an on-line gas chromatograph (GC). The temperature, pressure, feed rates, and sampling for GC analysis are controlled by a microprocessor and its relevant interface unit.

Polymerizations are carried out with the recipe

Table I   Propylene Polymerization Recipe

Chemical	Quantity
n-Heptane (mL)	2500
DEAC (g)	2.62
Catalyst (g)	0.5
Hydrogen (N mL)	1000
Initial molar ratio (propylene/H_2)	11.8
Propylene	Amount consumed at 6 atm constant pressure
Temperature (°C)	70
Pressure (atm)	6
Time (h)	2
Al/Ti (mol/mol)	6.4

Table II   Influence of Al/Ti Ratio on Yield and Polymer Properties

Al/Ti (mol/mol)	Aluminum Concentration (mol/L)	Yield (g PP[a]/g TiCl$_3$)	Average Rate (g PP/g TiCl$_3$-h)	II (% Wt)	BD (g/cm^3)	MFI (g/10 min)	d_{50} (μm)
2.6	3.3×10^{-3}	306	153	93.9	0.42	14	360
3.8	5.0×10^{-3}	392	196	94.9	0.44	18	425
6.4	8.3×10^{-3}	411	205	93.9	0.43	21	475
12.8	16.6×10^{-3}	378	189	96.6	0.42	20	520

[a] PP = polypropylene.

shown in Table I. The reactor is heated to 120°C and an approximately 10^{-3} mmHg vacuum is applied for 12 h to remove any trace impurities adsorbed on the reactor's internal surfaces. After this passivation step, the reactor is purged three times with propylene; then, the temperature is set to 65°C and n-heptane and propylene are fed to adjust the pressure of the reactor to 0.5 kg/cm^2 g. The agitation speed is adjusted to 200 rpm and the DEAC solution in n-heptane, which is prepared in the glove box, is transferred to the reactor with a special container. Then, the TiCl$_3 \cdot \frac{1}{3}$ AlCl$_3$, previously weighed in the glove box and put into a special capsule, is transferred into the reactor. After the catalyst addition, the reactor is closed, agitator speed is increased to 800 rpm, the required amount of hydrogen is fed, and heating of the reactor is started together with continuous feeding of propylene to keep the pressure of the reactor at 3 kg/cm^2 g. The heating rate is adjusted so that the reactor reaches 70°C in 5 min after catalyst addition. After the temperature reaches 70°C, the pressure of the reactor is adjusted to 6 kg/cm^2 g by feeding propylene. Propylene feeding under these conditions is continued for 2 h. Then, the unreacted monomer is vented and the polymer slurry is deactivated by adding butanol. The temperature is kept at 70°C during the catalyst deactivation and the slurry is agitated for 30 min. Then, the slurry is filtered and washed with heptane. The filtered wet cake is dried in a vacuum oven at 50°C, 760 mmHg vacuum for approximately 3 h. The solution obtained from filtration is kept for atactic polypropylene (APP) content determinations. During the polymerization, the consumptions of propylene and hydrogen are followed by a flow totalizer and by an on-line gas chromatograph, respectively.

Test Methods and Analytical Procedure

The quality of monomers, catalysts, and other chemicals used during experiments are checked in

line with their relevant test methods. Polypropylenes obtained from polymerizations are tested for various properties in line with the relevant test methods such as melt flow index (MFI) by ASTM-D 1238, bulk density (BD) by ASTM-D 1895, and dry sieve analysis by JISK 0069. The mean particle size (d_{50}) is determined by plotting the cumulative quantity of undersizes obtained from the JISK 0069 test on
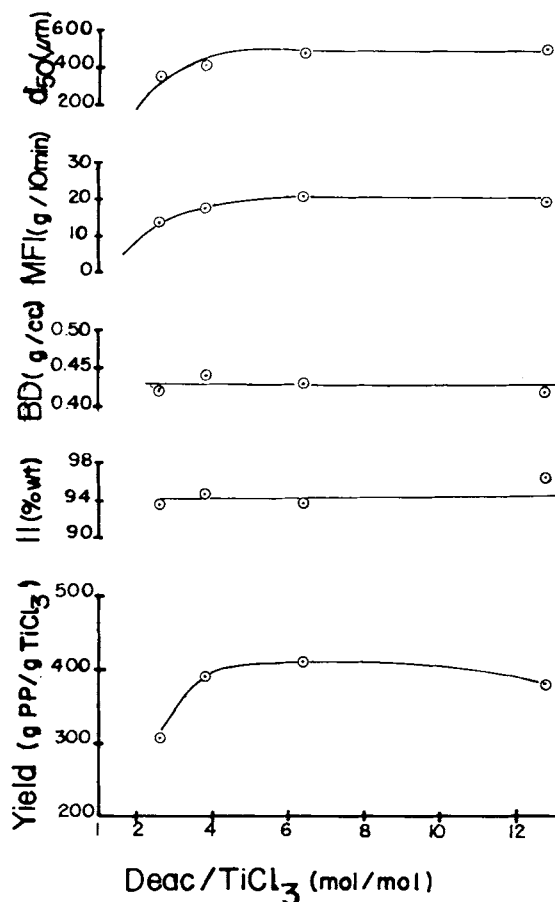
Deac/TiCl$_3$ (mol/mol)

Figure 2   Variation of yield and polymer properties with Al/Ti mol ratio, at 70°C, 6 atm with propylene/H$_2$ initial mol ratio 11.84; polymerization time 2 h.

Table III   Influence of Propylene (PP) Pressure on Yield and Polymer Properties

Pressure (atm)	Yield (g PP[a]/g TiCl$_3$)	Average Rate (g PP/g TiCl$_3$-h)	II (% Wt)	BD (g/cm^3)	d_{50} (μm)
4.0	271	135	93.4	0.44	420
6.0	426	213	94.4	0.44	500
9.0	591	295	94.3	0.46	620
12.0	777	388	94.5	0.45	700

[a] PP = polypropylene.

a probability paper. In addition, the particle size of product polypropylene is also determined by a laser diffraction technique using a Malvern 2600 C particle size analyzer. The isotactic index (II) of the product and the total amount of atactic polypropylene produced during polymerizations are determined by conventional analytical methods. Molecular weights of the polymers are determined by gel permeation chromatography (GPC) using a Waters 150 C instrument and 1,2,4-trichlorobenzene as the solvent.
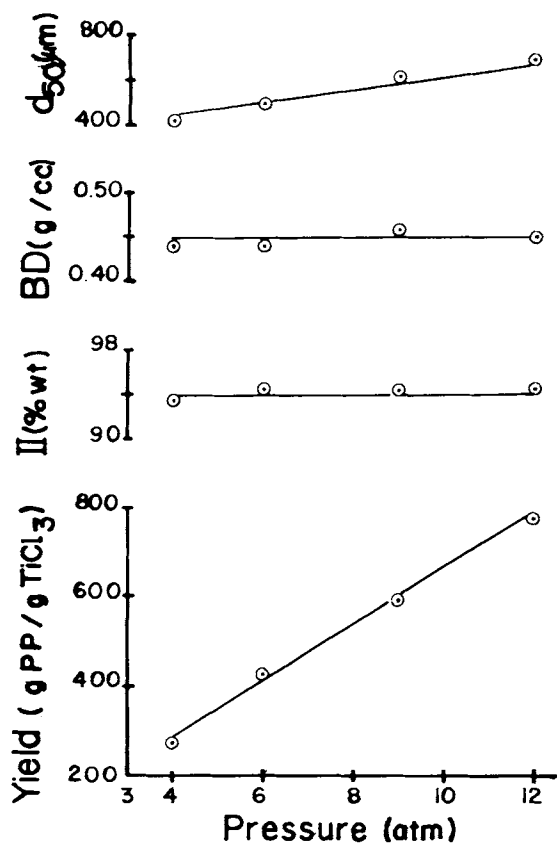

Figure 3   Variation of yield and polymer properties with polymerization pressure, at 70°C, Al/Ti mol ratio 6.4 with propylene/H$_2$ initial mol ratio 11.84; polymerization time 2 h.

RESULTS AND DISCUSSION

The recipe given in Table I is the standard recipe. To investigate the effects of various parameters, polymerizations are carried out by changing the tested parameter while keeping the others constant. The investigated parameters are the aluminum/titanium ratio, pressure, monomer concentration, temperature, hydrogen concentration, and duration of polymerization.

Elimination of the Effect of External Mass-transfer Resistance

To eliminate the effect of external mass-transfer resistance, the polymerization rate must be kept less than the rate of transport of gaseous propylene to
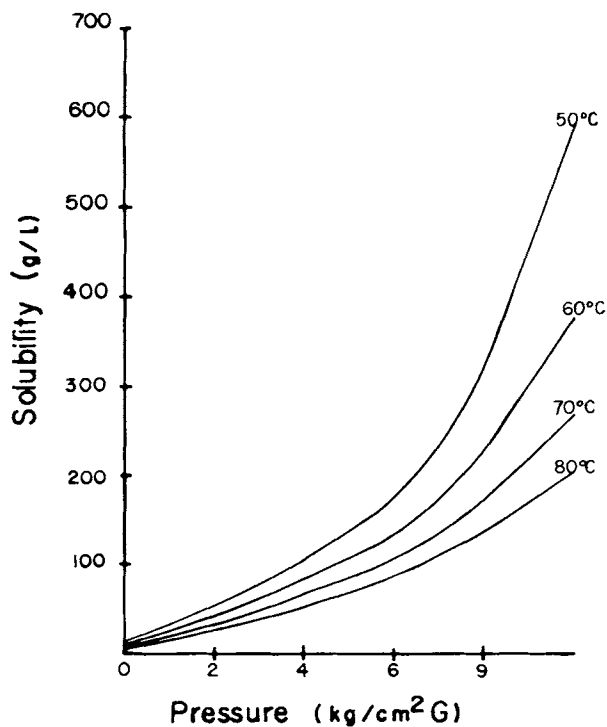

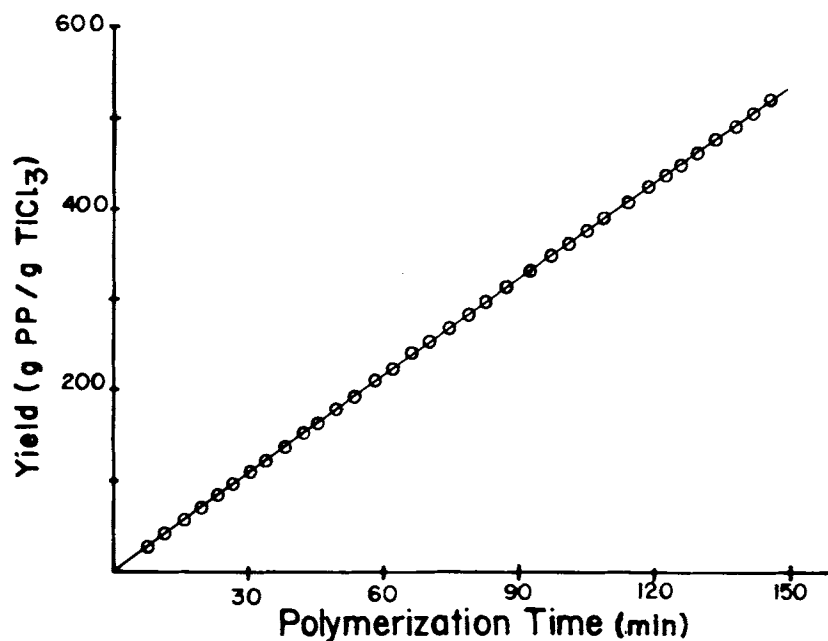Figure 4   Solubility of propylene in n-heptane calculated by Hysim process simulation software.

Figure 5 Variation of polymerization yield with polymerization time, at 70°C, 6 atm, Al/Ti mol ratio 6.4, and propylene/H_2 initial mol ratio 11.84.

the polymerization slurry. To investigate the effect of the external mass-transfer resistance, polymerization rates were measured by changing the stirring speed and the amount of the catalyst used. Above 200 rpm, the polymerization rate did not change at a catalyst concentration of 0.4 mmol/L. This result shows that there is no external mass-transfer resistance at this concentration when agitation speeds

are kept higher than 200 rpm. Above 200 rpm, the polymerization rate is linearly proportional to the amount of catalyst when the concentration of the catalyst in terms of Ti content is less than 1.6 mmol/L. Above 1.6 mmol/L catalyst concentrations, however, linearity is not obeyed. Since in our experiments a 0.4 mmol/L catalyst concentration and an 800 rpm agitation speed is used, it can easily be
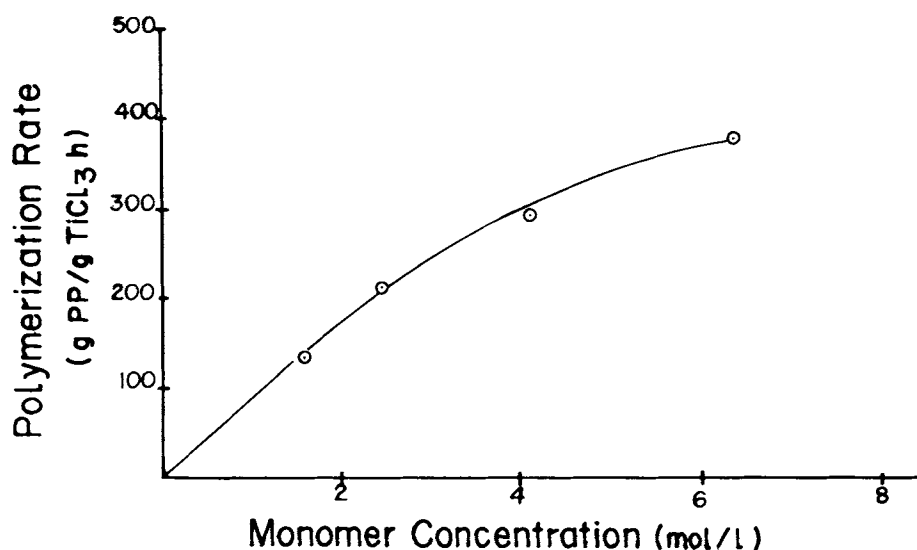

Figure 6 The dependence of rate of polymerization on monomer concentration, at 70°C, Al/Ti mol ratio 6.4 with propylene/H_2 initial mol ratio 11.84; polymerization time 2 h.

Table IV   Influence of Polymerization Temperature on Yield and Polymer Properties

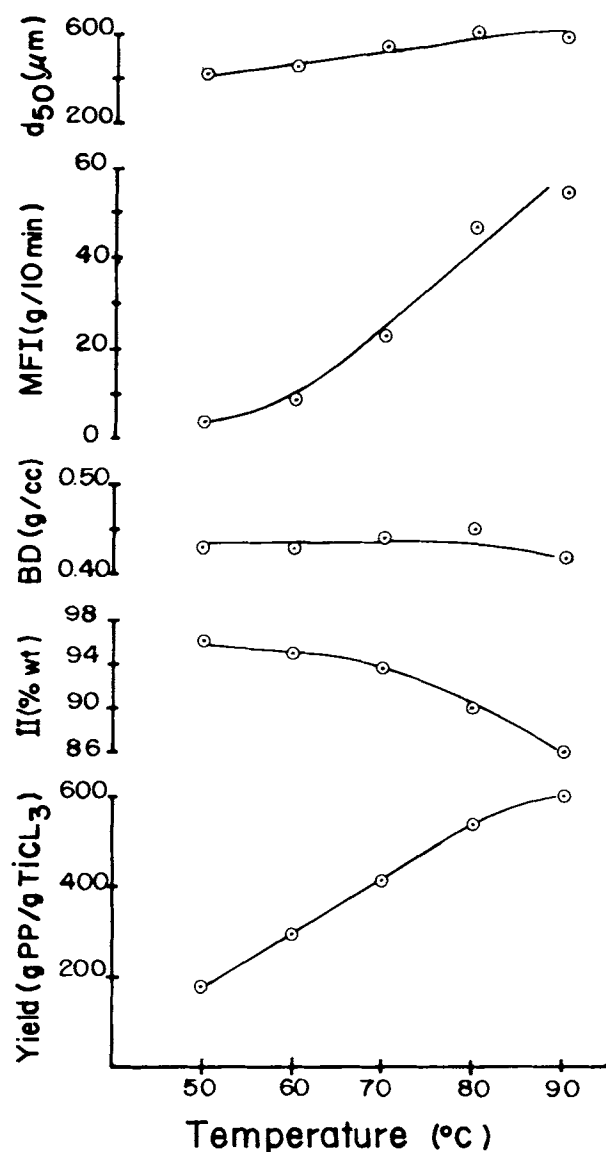| Temperature (°C)	Yield (g PP[a]/g TiCl$_3$)	Average Rate (g PP/g TiCl$_3$-h)	II (% Wt)	BD (g/cm^3)	MFI (g/10 min)	D_{50} (μm)
50	177	88	96.1	0.43	4	435
60	296	148	95.1	0.43	9	460
70	418	209	93.7	0.44	23	470
80	540	270	90.0	0.45	47	615
90	604	302	86.0	0.42	55	595

[a] PP = polypropylene.

Figure 7   Variation of yield and polymer properties with polymerization temperature, at Al/Ti mol ratio 6.4, 6 atm pressure with propyelene/H$_2$ mol ratio 11.84; polymerization time 2 h.

concluded that external gas–liquid transfer resistance is not a controlling parameter.

Effect of Aluminum/Titanium Ratio

The composition of the catalyst system represented by the Al/Ti molar ratio is an important reaction parameter in the polymerization of propylene. The variation of the Al/Ti ratio is investigated by keeping the amount of TiCl$_3$ constant and varying the amount of DEAC. The results are shown in Table II and Figure 2. As the ratio of aluminum to titanium is increased, the rate of polymerization initially increases, but a further increase in this ratio does not affect the polymerization rate. At the initial portion of the graph where rate of polymerization increases, polymer tacticity does not change with increasing Al/Ti ratio. Therefore, it suggests that the aluminum alkyl concentration is sufficiently high to saturate a considerable number of possible sites while an appreciable amount of it is used for scavenging trace quantities of impurities.

In the constant polymerization rate part of Figure 2, the increase in Al/Ti ratio does not affect the activity of the catalyst. It is seen that the product properties also do not change appreciably while the polymerization rate is constant.

When the Al/Ti ratio is further increased, activity seems to decrease, which can be attributed to the reactions of species such as ethylaluminum dichloride (EADC) resulting from active site formation and/or reaction of AlCl$_3$ in the catalyst with DEAC.[10]

Effect of Monomer Concentration

The effect of monomer concentration is investigated by conducting polymerizations at four different pressures: 4, 6, 9, and 12 kg/cm^2 g. The results obtained are shown in Table III and Figure 3.
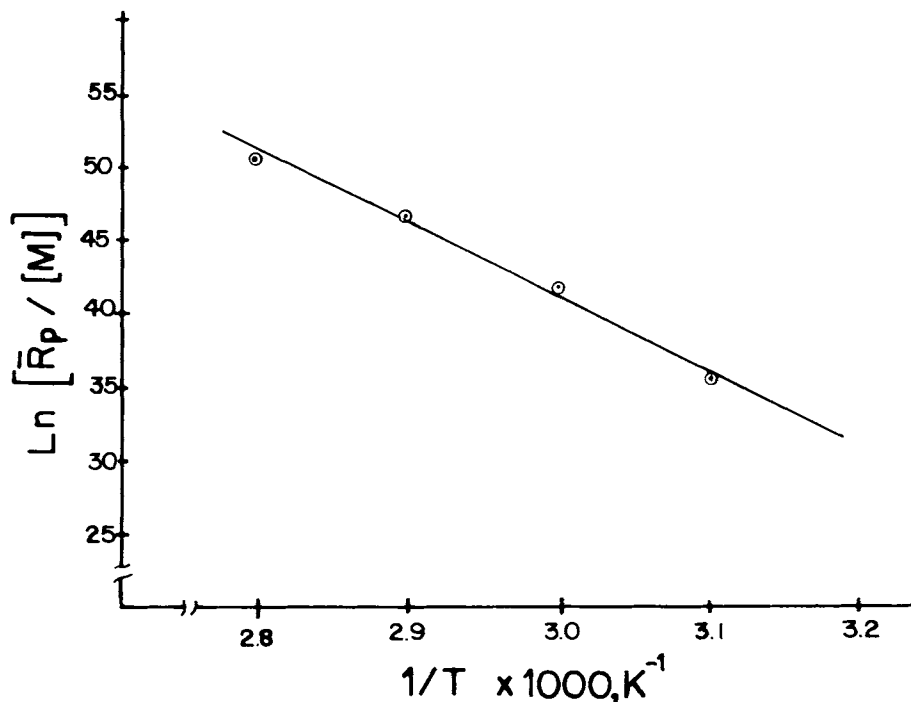
Figure 8 Arrhenius plot for slurry polymerization of propylene.

As seen from Figure 4, which is generated by computer on the basis of the Peng Robinson equation, making use of the Hysim Ver.2.10 Process Simulation Software of Hyprotech. The solubility of propylene gas increases with increasing propylene partial pressure. Therefore, the monomer concentration in the solvent increases as the propylene partial pressure increases.

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

$$R_p = K_p[C][M] \qquad (1)$$

where R_p is the rate of polymerization; K_p, the rate constant of propagation; and $[C]$, the concentration of active sites. Since the rate of polymerization is constant during the reaction, values of R_p could be obtained from the slope of the polymer yield vs. the time graphic, which is shown in Figure 5. The dependence of rate on the monomer concentration is shown in Figure 6. The rate of polymerization is found to be first order up to monomer concentrations of 2.5 mol/L.

As seen from Figure 3, when pressure, and, therefore, monomer concentration, increases, the yield, and, consequently, the mean particle size, increases while other polymer properties remain constant.

Effect of Polymerization Temperature

The effect of polymerization temperature is investigated in the temperature range between 50 and 90°C and the results obtained are shown in Table IV and Figure 7. Yield, and therefore polymerization rate, increases as temperature increases, but at temperatures above 80°C, a slight decrease in yield occurs. The mean particle size proportionally increases with yield, and bulk density stays almost unchanged up to 80°C. II remains almost the same between 50 and 70°C, but above ~ 70°C, polymer tacticity decreases considerably. MFI increases with temperature as a result of increased chain-transfer-agent effectiveness of hydrogen.

Table V Reported Activation Energies in Propylene Polymerization

Authors	Catalyst System	Ea (kcal/mol)
Natta et al.[11]	α-TiCl$_3$/TEA	10
Keii et al.[12-14]	TiCl$_3$/DEAC	13.5
Grigorev et al.[15]	TiCl$_3$/TEA	11.5–12.5
Yuan et al.[9]	α-TiCl$_3$·$\frac{1}{3}$AlCl3/DEAC	11.2
This work	TiCl$_3$·$\frac{1}{3}$AlCl3/DEAC	11.6

Table VI   Influence of Partial Pressure of Hydrogen on Yield and Polymer Properties

Hydrogen Feed (N mL)	Yield (g PP[a]/g TiCl₃)	Average Rate (g PP/g TiCl₃-h)	II (% Wt)	BD (g/cm³)	MFI (g/10 min)	d₅₀ (μm)
500	429	214	93.8	0.44	5	520
1000	419	209	94.4	0.44	19	500
2000	380	190	94.1	0.43	60	465

[a] PP = polypropylene.

An Arrhenius plot prepared from the data given in Table IV is shown in Figure 8. Note that the data of 90°C are not used for the Arrhenius plot, because of the deviation most probably due to the deactivation at this temperature. The overall activation energy estimated from the Arrhenius plot is in general agreement with several other workers, as shown in Table V.

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.[11] The effect of hydrogen is investigated at three hydrogen levels, keeping the total pressure of polymerization constant.

As seen from Table VI and Figure 9, yield, and, therefore, the polymerization rate, slightly decreases as hydrogen concentration increases. The rate decreases because hydrogen lowers the effective monomer concentration near catalytically active sites. The slight decrease in the polymerization rate was also observed by some previous investigators.[17,18] Hydrogen has a very pronounced effect on the molecular weight of the polymer obtained. The change of MFI by the molecular weight of the polymer is shown in Figure 10. The correlation between MFI and M is found to be in the below given form with correlation coefficient r of 0.998:

$$\log MFI = a - bM$$

Effect of Polymerization Time

The polymerization rate decreases by 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 data presented up to now were obtained from polymerizations carried out for 2 h. Experiments were carried out to better understand the rate decay behavior of the investigated catalyst system by elongating the time of polymerization to 6 h. The results obtained are shown in Table VII and in Figure 11.

As seen from Figure 11, the polymerization rate and particle size increase as a consequence of the
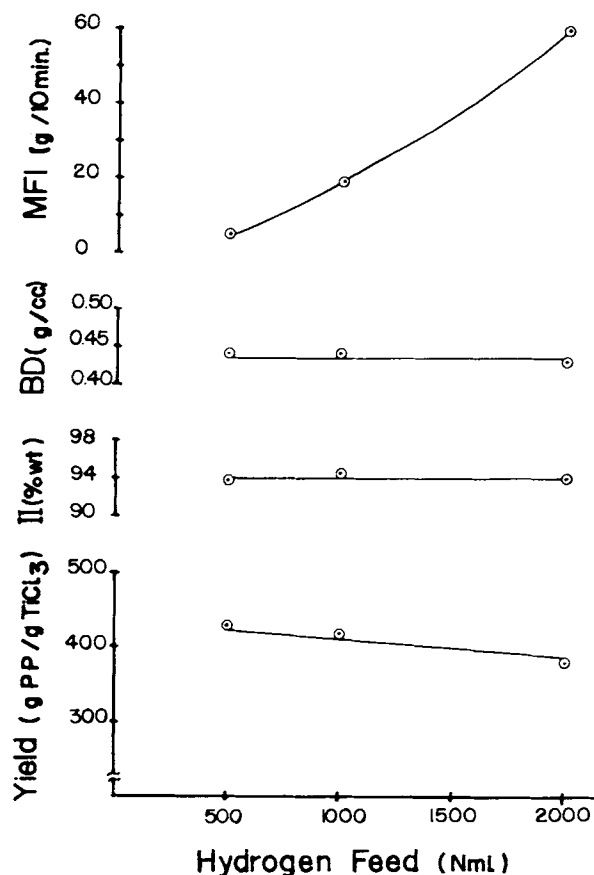

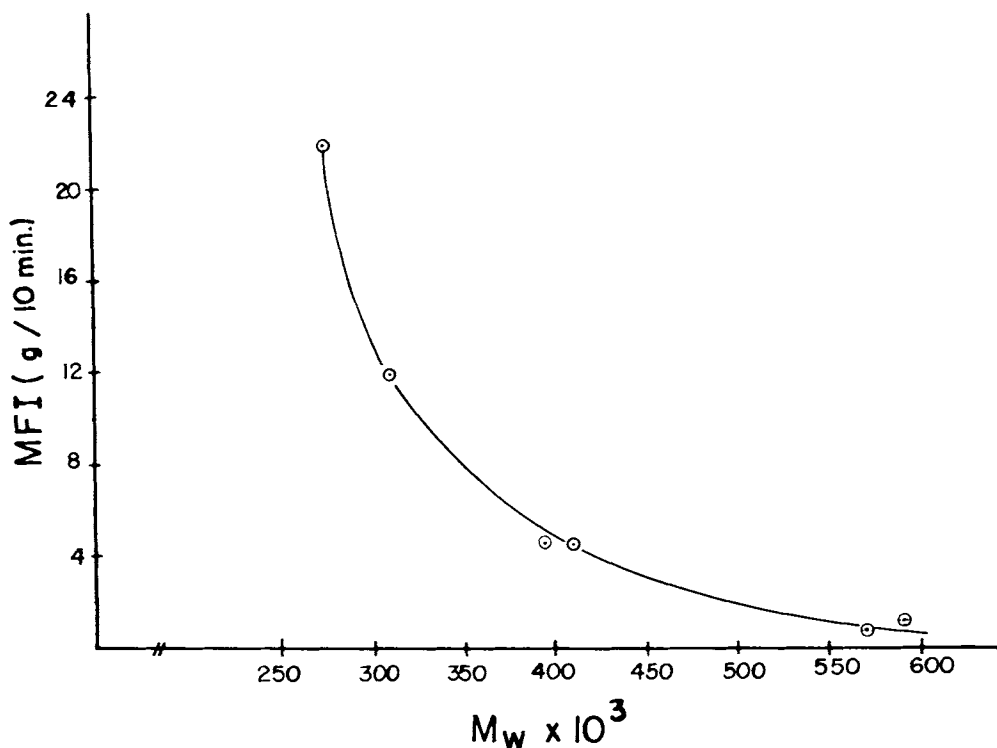**Figure 9**   Effect of hydrogen on yield and polymer properties.

Figure 10 The change of melt flow index by molecular weight of polymer.

increase of yield with time; the other resin properties stay unchanged. From the yield vs. the time graphic in Figure 11, it can be assumed that at the initial stages of the polymerization up to approximately 2.5–3 h the increase in yield is practically linear with time; thus, the polymerization rate can be assumed to be constant. From then on, the yield dependent on time starts to decrease due to a considerable decrease in polymerization rate. Since monomer concentration, temperature, and pressure are kept constant throughout these experiments, this can be attributed to either a change in active site concentrations [C^*] or the value of the overall reaction rate constant, K_p. However, was shown by other authors that the rate decay in the polymer-

ization of propylene is not due to formation of the polymer layer enveloping the catalyst particles and slowing down the monomer diffusion into the active sites, but is exclusively related to the interaction of the catalyst with an alkylaluminum compound. This reduces Ti^{3+} to lower oxidation states, mainly Ti^{2+}; therefore, the rate decreases.[10,18]

CONCLUSION

The studies of propylene polymerization approaching conditions of industrial relevance covering a wide range of parameters revealed the characteristics of the $TiCl_3/\frac{1}{3} AlCl_3$, $(C_2H_5)_2AlCl$ catalyst system. An

Table VII   The Variation of Yield and Polymer Properties with Polymerization Time

Time (h)	Yield (g PP[a]/g TiCl$_3$)	Average Rate (g PP/g TiCl$_3$-h)	II (% Wt)	Bulk Density (g/cm^3)	MFI (g/10 min)	d_{50} (μm)
1	220	220	93.3	0.43	30	435
2	426	213	94.4	0.43	22	555
4	655	164	94.5	0.42	11	710
6	912	152	93.2	0.43	9	720

[a] PP = polypropylene.
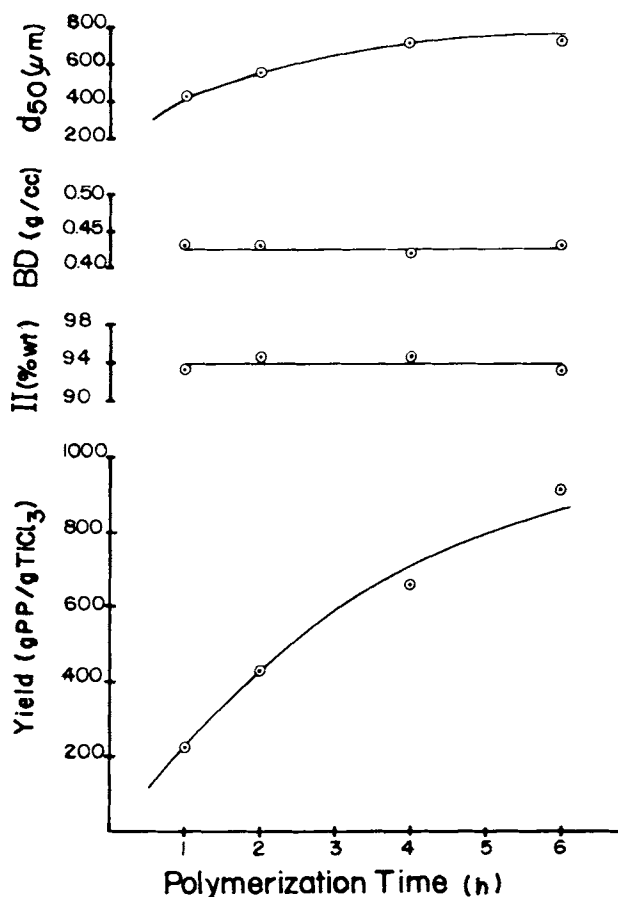
Figure 11   Variation of yield and polymer properties by time.

The isotactic index (II) and bulk density (BD) of the polymer obtained are not affected by the polymerization parameters, except that above 70°C, both BD and II decrease. The MFI of the propylene obtained changes by both temperature and hydrogen concentration, resulting in higher values as these parameter values are increased. As a general rule, independent of the parameter causing an increase in the yield, as yield increases, the mean particle diameter also increases.

Al/Ti ratio of 4.0–8.0 gives maximum yields; however, ratios higher than 8.0 inversely affect yield.

The rate of polymerization is first order in the investigated range of temperatures and pressures up to 2.5 mol/L monomer concentrations provided that the polymerization time is limited to 2 h. Temperatures covered are 40–90°C and pressures of 4–12 kg/cm², corresponding to 1.6–6.4 mol/L monomer concentrations. As temperature increases, the polymerization rate and yield increases; however, above 80°C, a slight decrease in yield occurs.

Hydrogen, as expected, acts as a very effective chain-transfer agent; therefore, increased amounts of it increases MFI and thus reduces molecular weight. A good correlation between MFI and molecular weight exists. In addition, at increased amounts of hydrogen concentrations, a slight decrease in the polymerization rate occurs. The polymerization rate decay profile reveals approximately constant rates up to 2 h, followed by a decay by time.

REFERENCES

1. T. Nozaki and J. C. W. Chien, *J. Polym. Sci., Polym. Chem. Ed.,* **29,** 1807–1817 (1991).
2. J. C. W. Chien and T. Nozaki, *J. Polym. Sci. Polym. Chem. Ed.,* **29,** 505–514 (1991).
3. X. Zhou, S. Lin, and J. C. W. Chien, *J. Polym. Sci. Polym. Chem. Ed.,* **28,** 2609–2632 (1990).
4. J. C. W. Chien and Y. Hu, *J. Polym. Sci. Polym. Chem. Ed.,* **25,** 2881–2892 (1987).
5. M. Kakugo, T. Miyatake, Y. Naito, and K. Mizunuma, *Macromolecules,* **21,** 314–319 (1988).
6. M. Antberg, V. Dolle, S. Haftka, J. Rohrmann, W. Spaleck, A. Winter, and H. J. Zimmermann, *Makromol. Chem. Macromol. Symp.,* **48/49,** 333–347 (1991).
7. K.-S. Kang, M.-A. Ok, and S.-K. Ihm. *J. Appl. Polym. Sci.,* **40,** 1303–1311 (1990).
8. J. C. W. Chien, *J. Polym. Sci. Polym. Chem. Ed.,* **1,** 425–442 (1963).
9. H. G. Yuan, T. W. Taylor, K. Y. Choi, and W. H. Ray, *J. Appl. Polym. Sci.,* **27,** 1691–1706 (1982).
10. V. W. Buls and T. L. Higgins, *J. Polym. Sci. Polym. Chem. Ed.,* **11,** 925–938 (1973).
11. G. Natta, G. Mazzanti, P. Longi, and F. Bernadin, *Chim. Ind. (Milan),* **41,** 519 (1959).
12. T. Keii and Y. Doi, *Asahi Glass Kogyogijitsu Shoreikai Rep.,* **29,** 95 (1976).
13. Y. Doi, Y. Yoshimoto, and T. Keii, *Nippon Kagaku Zasshi,* **3,** 495 (1972).
14. Y. Doi, H. Kobayashi, and T. Keii, *Nippon Kagaku Zasshi,* **N6,** 1089 (1973).
15. V. A. Grigorev, V. I. Pilipovskii, Z. V. Arkhipova, E. V. Eroteev, and G. A. Fedina, *Int. Polym. Sci. Tech.,* **1**(5), 73 (1974).
16. I. Okura, A. Kojima, K. Soga, and T. Keii, *J. Polym. Sci.,* **8,** 2717 (1970).
17. K. Y. Choi, and W. H. Ray, *J. Appl. Polym. Sci.,* **30,** 1065–1081 (1985).
18. V. Busico, *Makromol. Chem.,* **187,** 1125–1130 (1986).