

Polymerization of Propylene Using the High-Activity Ziegler–Natta Catalyst System SiO₂/MgCl₂ (Ethoxide Type)/TiCl₄/Di-*n*-butyl Phthalate/Triethylaluminum/Dimethoxy Methyl Cyclohexyl Silane

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ABSTRACT: The bisupported Ziegler–Natta catalyst system SiO₂/MgCl₂ (ethoxide type)/TiCl₄/di-*n*-butyl phthalate/triethylaluminum (TEA)/dimethoxy methyl cyclohexyl silane (DMMCHS) was prepared. TEA and di-*n*-butyl phthalate were used as a cocatalyst and an internal donor, respectively. DMMCHS was used as an external donor. The slurry polymerization of propylene was studied with the catalyst system in *n*-heptane from 45 to 70°C. The effects of the TEA and H₂ concentrations, temperature, and monomer pressure on the polymerization were investigated. The optimum productivity was obtained at [Al]/[DMMCHS]/[Ti] = 61.7:6.2:1 (mol/mol/mol). The highest activity of the catalyst was obtained at 60°C. Increasing the H₂ concentration to 100 mL/L increased the productivity of the catalyst, but a further increase in H₂ reduced the activity of the catalyst.

Increasing the propylene pressure from 1 to 7 bar significantly increased the polymer yield. The isotacticity index (II) decreased with increasing TEA, but the H₂ concentration, temperature, and monomer pressure did not have a significant effect on the II value. The viscosity-average molecular weight decreased with increasing temperature and with the addition of H₂. Three catalysts with different Mg/Si molar ratios were studied under the optimum conditions. The catalyst with a Mg/Si molar ratio of approximately 0.93 showed the highest activity. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1177–1181, 2003

Key words: Ziegler–Natta polymerization; supports; poly(propylene) (PP)

INTRODUCTION

The manufacture of high-activity catalysts for polymerizing propylene requires a support that stabilizes the active centers of the catalysts. A variety of metal halides and oxides have been reported as suitable supports for the catalysts.^{1–3} Anhydrous MgCl₂ has been known as a preferred support for highly efficient Ziegler–Natta catalysts for the polymerization of olefins. MgCl₂, which is usually used, is often inconvenient because of the high decay rate of the polymerization activity. However, it is a good support for the preparation of highly active Ziegler–Natta catalysts. The most important step is the preparation of spherical MgCl₂, but this process is rather complicated and not easy to control.^{4,5} Inorganic oxides, such as SiO₂ and Al₂O₃, have also been used as catalyst supports because of their high specific surface areas and good morphology.^{6,7} However, SiO₂-supported titanium catalysts show low activity and yield polypropylene (PP) with low isotacticity.^{8,9}

SiO₂/MgCl₂-bisupported TiCl₄ catalysts have been used for the polymerization of ethylene and propylene and for their copolymerization. The bisupported catalysts are very suitable for controlling the particle sizes of polymers.^{6,7,10–12} Many SiO₂/MgCl₂-bisupported Ti catalysts have been reported, but most of them have been used for ethylene polymerization.^{11,13} Only a few of the catalysts have been related to the polymerization of propylene.^{6,9,13} With the catalyst system SiO₂/MgCl₂/TiCl₄/internal donor, the polymerization rate increases with time, whereas for the MgCl₂/TiCl₄/internal donor catalyst, a decay-type curve can be obtained.⁶

There exist both chemical bonding and physical interactions between SiO₂ and MgCl₂ supports. The activities in propylene polymerization reactions remarkably increase with increasing Mg/Ti molar ratios in the catalysts, whereas in ethylene polymerization, the activity mainly depends on the Ti content in the catalyst and on the calcination temperature of SiO₂.^{2,13}

SiO₂ has even been used as a support for metallo-cene Ni-based and Fe-based catalysts, a new generation of Ziegler–Natta catalysts reported to have single active sites.^{13–16}

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In our laboratory, we combined $\text{Mg}(\text{OEt})_2$ with calcinated SiO_2 and TiCl_4 as a catalyst (in the presence of dimethoxy methylcyclohexyl silane as the internal donor) to improve the activity of the bisupported catalyst system $\text{SiO}_2/\text{MgCl}_2/\text{TiCl}_4/\text{dimethoxy methyl cyclohexyl silane}$ (DMMCHS) for the polymerization of propylene.

EXPERIMENTAL

Magnesium ethoxide was supplied by Aldrich Chemicals Co., Ltd. (Old Brickyard, UK), and was used as received. SiO_2 was supplied by Kerman Rubber Industry (Kerman, Iran) and was calcinated at 520–560°C for approximately 4 h before use. Titanium tetrachloride was obtained from Merck Chemical Co., Ltd. (Darmstadt, Germany), and triethylaluminum (TEA) was acquired from Schering Co., Ltd. (Bergkman, Germany). DMMCHS was supplied by Arak Petrochemical Co. (Arak, Iran). Di-*n*-butyl phthalate and toluene were obtained from Merck Chemicals and were stored over activated 13× and 4-Å molecular sieves. *n*-Heptane and *n*-hexane were supplied by Arak Petrochemical and were distilled over calcium hydride and stored over 13× and 4-Å activated molecular sieves and sodium wire. Decaline of 97% purity was supplied by Aldrich Chemical and was used with an antioxidant (0.1% 2,6-di-*tert*-butyl-*p*-cresol). Polymerization-grade propylene (purity > 99.9%) was supplied by Tabriz Petrochemical Co. (Tabriz, Iran) and was purified by passage through a column of activated 13× and 4-Å molecular sieves. Nitrogen gas (purity = 99.99%) was supplied by Nirogas Co. (Tehran, Iran) and dried by passage through P_2O_5 , KOH and activated silica gel and 4-Å molecular sieve columns.

SiO_2 was calcinated at 520–560°C for 4 h; 5 g of the calcinated SiO_2 and 10 g of $\text{Mg}(\text{OEt})_2$ (0.087 mol) were transferred in a glove box into a catalyst preparation reactor. Toluene (120 mL) was added to the reactor under a flow of dry N_2 . The content of the reactor was heated to 80°C in an oil bath. TiCl_4 (30 mL) was added while the contents of the reactor were stirred. The temperature was raised to 115°C, at which point 2.7

TABLE I
Effect of TEA Concentration on Polymerization

TEA (mmol)	[Al]/[Ti] molar ratio	Yield (g of PP/mmol of Ti)	II (%)
2.5	20.6	54.32	97.4
5	41.2	120.25	97.15
7.5	61.7	152.26	95.92
10	82.3	117.69	95.64
12.5	102.7	115.23	95.47

Temperature = 60°C; [Ti] = 12.15×10^{-2} mmol/L; polymerization time = 2 h.

TABLE II
Effect of H_2 on Polymerization

H_2 (mL/L)	Yield (g of PP/mmol of Ti)	II (%)	M_v
0	152.26	95.92	9.3×10^5
25	165.43	96.95	—
50	175.64	95.15	—
75	206.58	94.20	—
100	281.81	95.32	3.82×10^5
125	217.86	—	—
150	188.23	—	—

[Al]/[DMMCH]/[Ti] = 61.7:6.2:1, temperature = 60°C; polymerization time = 2 h; monomer pressure = 1 bar; [Ti] = 12.15×10^{-2} mmol/L.

mL (0.01 mol) of di-*n*-butyl phthalate was added under vigorous stirring. Then, the contents of the reactor were filtered, the solid product was washed twice with toluene (2×100 mL), and 120 mL of toluene and 30 mL of TiCl_4 were added. The reaction was carried out for 4 h at 115°C. The liquid in the reactor was filtered off, and the solid catalyst was washed with dry *n*-heptane at 60°C. The catalyst (SMT-1) was then dried at 70°C under a flow of N_2 .

Catalysts SMT-2 and SMT-3 were prepared with the same method used for the preparation of the SMT-1 catalyst, but the Mg/Si ratios were 0.47 and 2.06, respectively.

Propylene polymerization reactions were carried out in accordance with ref. 12. The isotacticity index (II) and the viscosity-average molecular weight (M_v) of some polymers were determined according to refs. 17 and 18, respectively.

RESULTS AND DISCUSSION

Effect of the TEA concentration

Polymerization reactions were conducted with SMT-1 at various Al/Ti molar ratios and at a constant titanium concentration for the establishment of the optimum activity. Slurry polymerizations were carried out in 400 mL of dry *n*-heptane at 60°C, at a titanium concentration of 0.125 mol/L, with 1 bar of pressure of propylene for 2 h. Table I shows the results of the polymerization reactions. Increasing the Al/Ti molar ratio from 20.6:1.0 to 61.7:1.0 increased the productivity of the catalyst, whereas a further increase in the ratio reduced the productivity. The II value of the polymer slightly decreased with an increasing ratio. Similar results were reported earlier.^{12,19} TEA alkylates active centers of the catalyst and reduces Ti from Ti^{4+} to Ti^{3+} and Ti^{2+} . When the concentration of TEA was increased above the optimum value, an overreduction of Ti^{4+} to Ti^{2+} occurred.²⁰

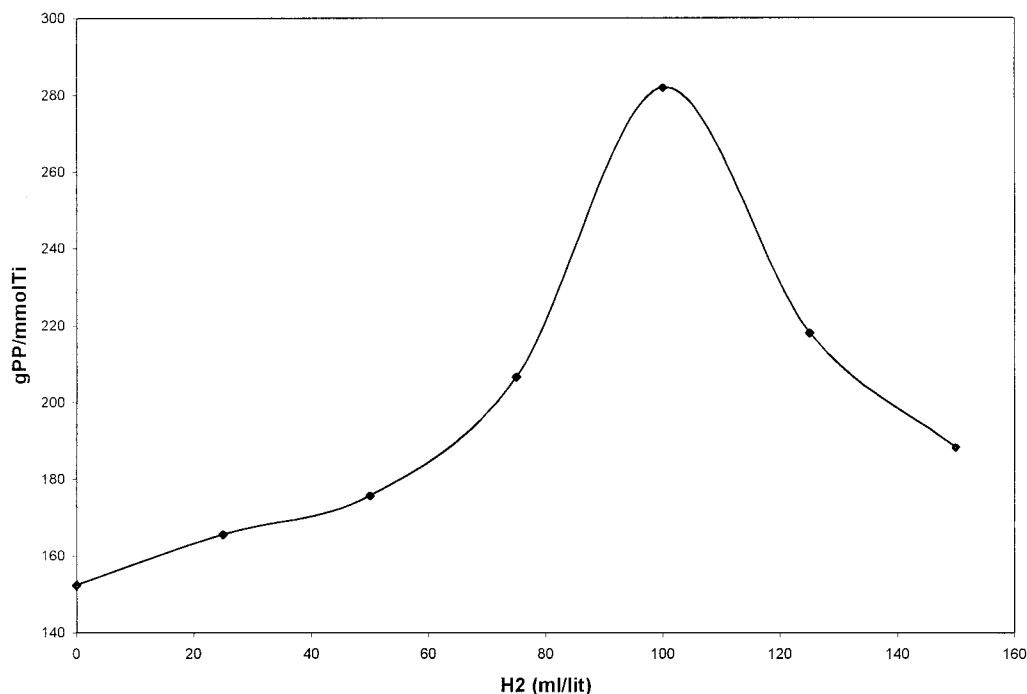


Figure 1 Effect of H₂ on the polymer yield.

Effect of the H₂ concentration

Different amounts of H₂ were used as a chain-transfer agent 2 min after the TEA addition. The optimum productivity of the catalyst was obtained with 100 mL/L H₂. The catalyst productivity, compared with polymerization in the absence of hydrogen, increased up to two times with the addition of hydrogen (Table II). Figure 1 shows the effect of H₂ on the polymerization behavior of the catalyst. M_v of the polymer sharply decreased in the presence of H₂. However, H₂ did not significantly affect II. The most likely explanation for the behavior is that H₂ activates some dormant centers in the catalyst.^{21–23} There is another hypothesis, based on the oxidation of Ti²⁺ sites that are not active for the polymerization of propylene: with the addition of H₂, the oxidation of the sites may take place.³

Hydrogen is the most widely used chain-transfer agent for molecular weight control in industrial prac-

tice with Ziegler–Natta systems. A considerable activity enhancement effect of hydrogen has been observed in the polymerization of propylene with MgCl₂-supported^{24–26} and EB/ZrCl₂-MAO catalyst systems.²³

Temperature effect

The polymerization reactions were carried out from 45 to 70°C with the optimum H₂ concentration and Al/Ti molar ratio. The highest yield was obtained at 60°C (Table III). M_v and II decreased with increasing temperature. Similar results were previously reported.^{26–28} An increase in the values of the propagating rate constant with increasing temperature and an irreversible deactivation of active sites at high temperatures was reported earlier.^{2,3,17} The solubility of the monomer and H₂ decreased at high temperatures, and this could affect the polymerization rate as well.

TABLE III
Effect of Temperature on Polymerization

Temperature (°C)	Yield (g of PP/mmol of Ti)	M_v	II (%)	T_m (°C)
45	164.11	9.3×10^5	97.96	162.08
55	240.16	4.2×10^5	95.45	163.63
60	281.81	3.8×10^5	95.32	164.93
65	163.70	—	—	—
70	83.54	—	94.74	165.98

[Al]/[DMMCH]/[Ti] = 61.7:6.2:1; [H₂] = 100 mL/L; polymerization time = 2 h; monomer pressure = 1 bar; [Ti] = 12.15×10^{-2} mmol/L. T_m = melting temperature.

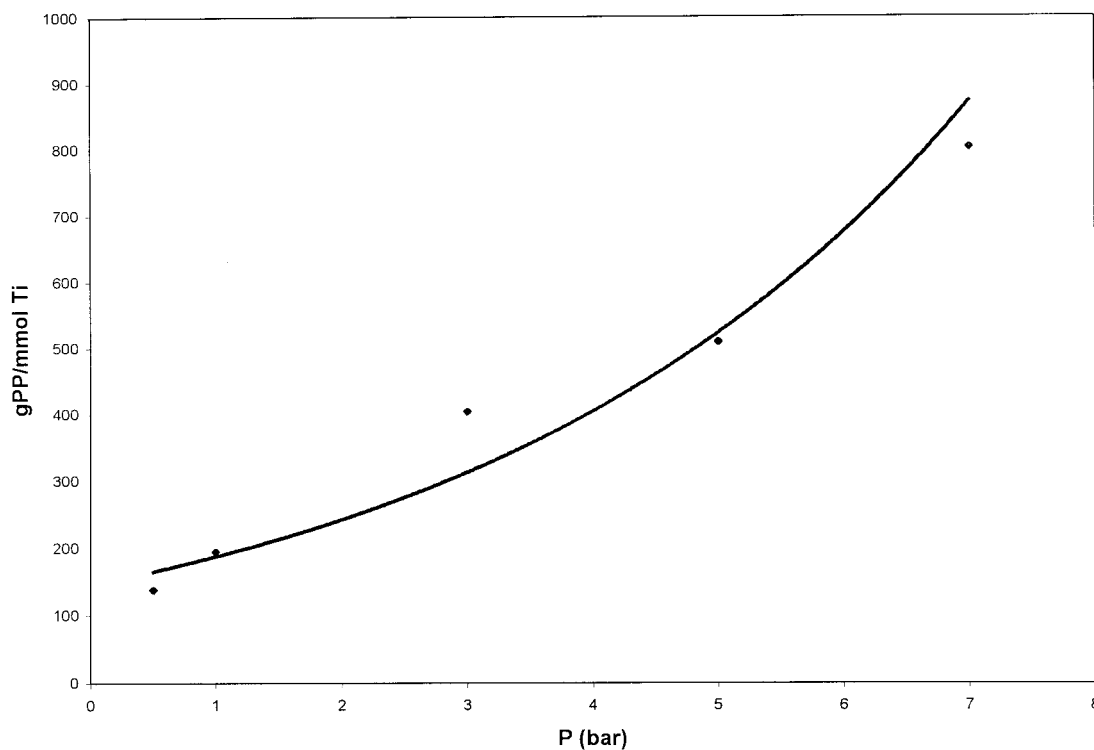


Figure 2 Effect of the monomer pressure P on the catalyst productivity.

Effect of the monomer pressure

Monomer pressures of 1–7 bar were studied under the optimum conditions previously determined. Figure 2

shows the productivity of the catalyst versus the monomer pressure. Increasing the monomer pressure sharply increased the catalyst productivity because of the higher concentration of the monomer. The first-

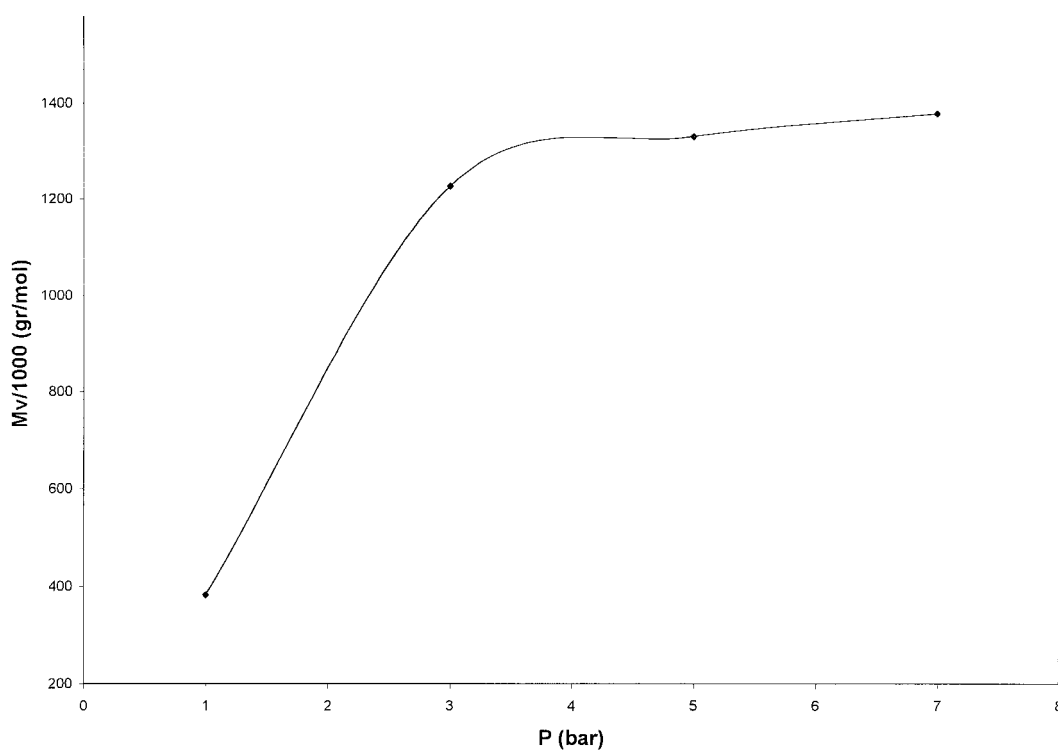


Figure 3 Effect of the monomer pressure P on M_v .

TABLE IV
Effect of Mg/Si Molar Ratio on Polymer Productivity

Catalyst	Mg/Si (molar ratio)	Ti (mmol)	Yield (g of PP/mmol of Ti)
SMT-1	0.93	0.1215	281.81
SMT-2	0.47	0.1048	5.72
SMT-3	2.06	0.1340	19.40

order rate of polymerization with the propylene concentration has been reported for Ziegler-Natta catalysts.^{17,28,29} However, a reaction rate order higher than the first has been reported for the polymerization of olefin with metallocenes catalysts.³⁰⁻³²

M_v of the polymer was significantly increased with the monomer pressure increasing from 1 to 3 bar, whereas a further increase of the pressure to 7 bar did have not much of an effect on the M_v value (Fig. 3). This behavior could be due to a higher concentration of the monomer at active sites, which could, in effect, reduce the role of the chain-transfer reaction to H₂ and TEA.

Effect of the mg/si molar ratio on the catalyst productivity

Three catalysts with different Mg/Si molar ratios were prepared. The polymerization reactions were carried out with the optimum conditions obtained for catalyst SMT-1. The highest productivity of the catalysts was obtained at a Mg/Si molar ratio of 0.93. Table IV shows the polymerization results.

CONCLUSIONS

1. There was an optimum Al/Ti molar ratio with respect to the yield of the polymer.
2. Increasing the H₂ concentration to 100 mL/L increased the productivity of the catalyst, but a higher concentration reduced the productivity.
3. Increasing the TEA and H₂ concentrations and temperature reduced the II value.
4. Polymerization reactions from 45 to 70°C were studied. The highest productivity was obtained at 60°C.
5. Increasing the temperature reduced M_v , whereas increasing the monomer pressure to 7 bar gave polymers with higher M_v values.
6. The productivity of the catalyst significantly increased with the monomer pressure.

7. The highest activity was obtained at a Mg/Si molar ratio of 0.93.

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