

Comparative Study of Propylene Polymerization Using Monosupported and Bisupported Titanium-Based Ziegler–Natta Catalysts

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ABSTRACT: Heterogeneous Ziegler–Natta systems—MgCl₂ (ethoxide type)/TiCl₄/di-*n*-butyl phthalate (DNBP)/triethylaluminum (TEA)/dimethoxymethylcyclohexylsilane (DMMCHS) and SiO₂/MgCl₂ (ethoxide type)/TiCl₄/DNBP/TEA/DMMCHS—were studied for the polymerization of propylene. The slurry polymerization of propylene was carried out with the catalyst systems in *n*-heptane. Both systems performed with optimum activity at a particular [Al]/[DMMCHS]/[Ti] molar ratio. The ratio to reach the highest activity was much lower for the bisupported catalyst system. The productivity of the bisupported catalyst was higher than that of the monosupported one. Polypropylene of a high isotacticity index (II; >96%) was obtained with both systems and did not significantly change with an increasing [Al]/[DMMCHS]/[Ti] molar ratio. The addition of hydrogen as a chain-transfer agent reduced II of the poly-

mers obtained with both systems. The effect of the polymerization temperature (40–75°C) on the viscosity-average molecular weight (M_v) and II showed a decrease in both cases. The bisupported catalyst system produced a polymer with higher M_v . The effect of temperature on II was similar for both the monosupported and bisupported systems. A monomer pressure of 2.02×10^5 to 0.8×10^6 Pa increased M_v of the obtained polymer. II of the polymer slightly decreased with increasing monomer pressure. The titanium content of the catalyst was 1.70 and 3.55% for the monosupported and bisupported systems, respectively. The surface area of the bisupported catalyst was higher than that of the monosupported catalyst. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2220–2226, 2006

Key words: catalysts; poly(propylene) (PP); supports

INTRODUCTION

Polyolefins are commercially produced with classical heterogeneous Ziegler–Natta catalysts on MgCl₂ supports, with chromium catalysts on SiO₂ or Al₂O₃ supports, which are better known as Philips catalysts, and with metallocene-based catalysts.¹ The discovery of high-yield δ -MgCl₂-supported catalysts for the polymerization of ethylene and then propylene in 1975 was an explosion in the field of catalyst polymerization of olefins. Since then, a number of catalysts and supports have been used for the polymerization of ethylene and propylene.^{2–4}

Homogeneous catalysts, including the new systems of Brookhart et al.⁵ and Gibson and coworkers,^{6–8} and metallocene^{1,9–11} and FI catalysts¹² have resulted in serious fouling of reactors in the slurry process. In general, reactor fouling can be avoided in the slurry and gas-phase process by heterogenization of the catalyst through support on suitable carriers. Homogeneous catalysts are usually supported on inorganic

and organic materials.^{1,10,13} For late-transition-metal catalysts, silica and silica/alumina derivatives have been used as carriers in preparing supported catalysts as well.¹³ Even in new-generation catalysts (metallocene, postmetallocene, and FI catalysts), SiO₂ as a support plays an important role, mainly in reducing fouling of the polymerization systems. The success of metallocenes mainly depends on the fact that modern polypropylene (PP) technologies and gas-phase plants and slurry-reactor plants can be used for heterogeneous metallocene catalysts.^{1,14} This will certainly speed up the replacement of PP produced by Ziegler–Natta catalysts.

The major objective of the heterogenization process is, on the one hand, to preserve the advantages of homogeneous systems, such as the high versatility and flexibility of the corresponding synthesis, the ability to control the polymer microstructure, and their high activity. On the other hand, it is intended to combine these features with the properties of supported catalyst technologies (good morphology, little reactor fouling, and high powder density).¹

MgCl₂-supported TiCl₄ catalysts have exhibited activities 2 orders of magnitude greater than those of Ziegler–Natta original catalysts and generated high-

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TABLE I
Titanium Content and Surface Area of the Catalysts

Catalyst	Ti content (%)	Surface area (m ² /g)
Bisupported	3.53	233
Monosupported	1.70	177

performance high-density polyethylene, linear low-density polyethylene, and highly isotactic PP, for example.¹²

SiO₂ is known to be an ideal support with good morphology and thermostability for the preparation of industrial olefin catalytic polymerization.¹⁵ Amorphous and porous SiO₂ at present constitutes the best support for metallocenes and methylaluminoxane (MAO) as a cocatalyst because it possesses a high surface area and porosity, has good mechanical properties, and is stable and inert under reaction and processing conditions.^{16,17} As a result of immobilization, the metallocene/MAO molar ratio can be reduced by approximately 2 orders of magnitude in comparison with homogeneous systems.^{18,19} Heterogenization increases the complexity of catalyzed systems as adds the influence of the support and the supporting method. Nevertheless, both MgCl₂ and SiO₂ are still the main supports on scientific and industrial scales.²

EXPERIMENTAL

The materials, catalyst preparation methods, polymerization procedures, and characterization methods have been explained elsewhere.^{20–22}

RESULTS AND DISCUSSION

Two heterogeneous Ziegler–Natta catalyst systems—MgCl₂ (ethoxide type)/TiCl₄/di-*n*-butyl phthalate (DNBP)/triethylaluminum (TEA)/dimethoxymethylcyclohexylsilane (DMMCHS), a monosupported catalyst, and SiO₂/MgCl₂(ethoxide type)/TiCl₄/DNBP/TEA/DMMCHS, a bisupported catalyst—were prepared.^{20–22} The SiO₂/MgCl₂ molar ratio of 1:1 was chosen for the bisupported catalyst. Table I gives analytical details for the two catalysts. The amount of Ti loaded onto the bisupported system was higher. The behavior could be due to hydroxyl groups present on the surface of SiO₂, which readily reacted with TiCl₄.

The slurry polymerization of propylene was studied with the catalyst systems in *n*-heptane. An optimum activity was obtained in terms of the [Al]/[Ti] molar ratio for both catalyst systems. Figure 1 shows the polymerization activity against the [Al]/[Ti] molar ratio. The highest activities were obtained at [Al]/[Ti] = 209:1 and [Al]/[Ti] = 62:1 for the monosupported and bisupported catalysts, respectively. The bisup-

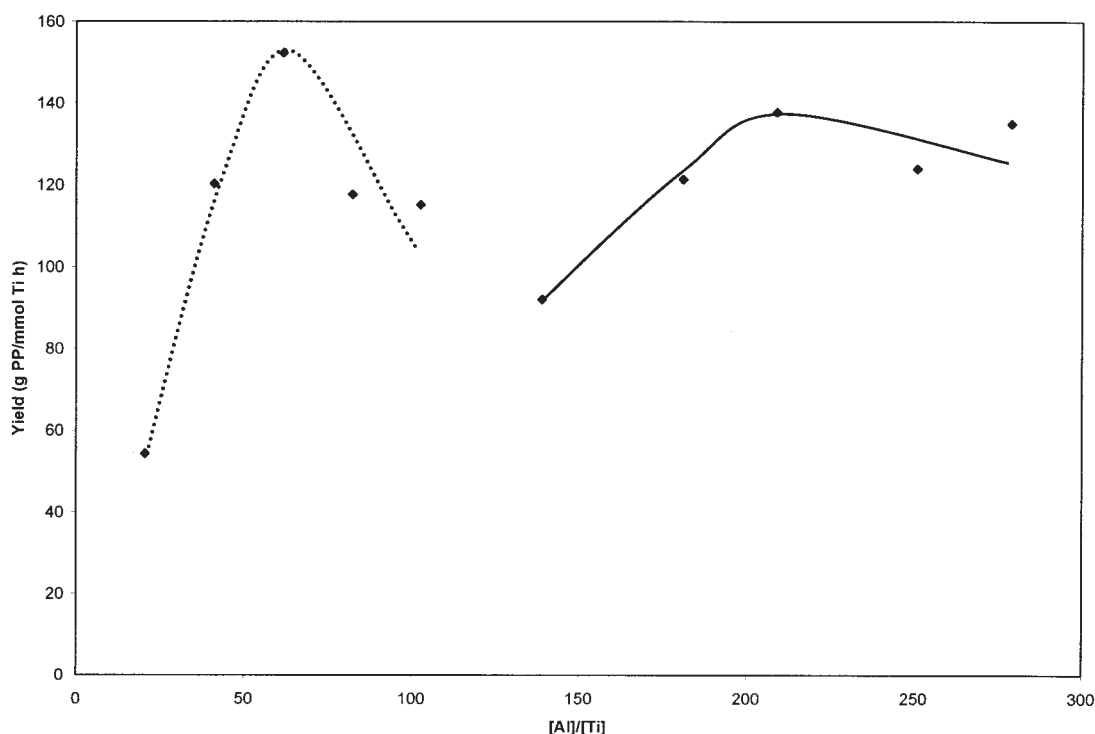


Figure 1 Effect of the [Al]/[Ti] molar ratio on the yield of propylene (polymerization conditions: temperature = 60°C, monomer pressure = 2.02×10^5 Pa, and polymerization time = 2 h): (· · ·) bisupported catalyst ([Ti] = 0.12 mmol/L, [DMMCHS] = 0.75 mmol/L) and (—) monosupported catalyst ([Ti] = 0.18 mmol/L, [DMMCHS] = 3.60 mmol/L).

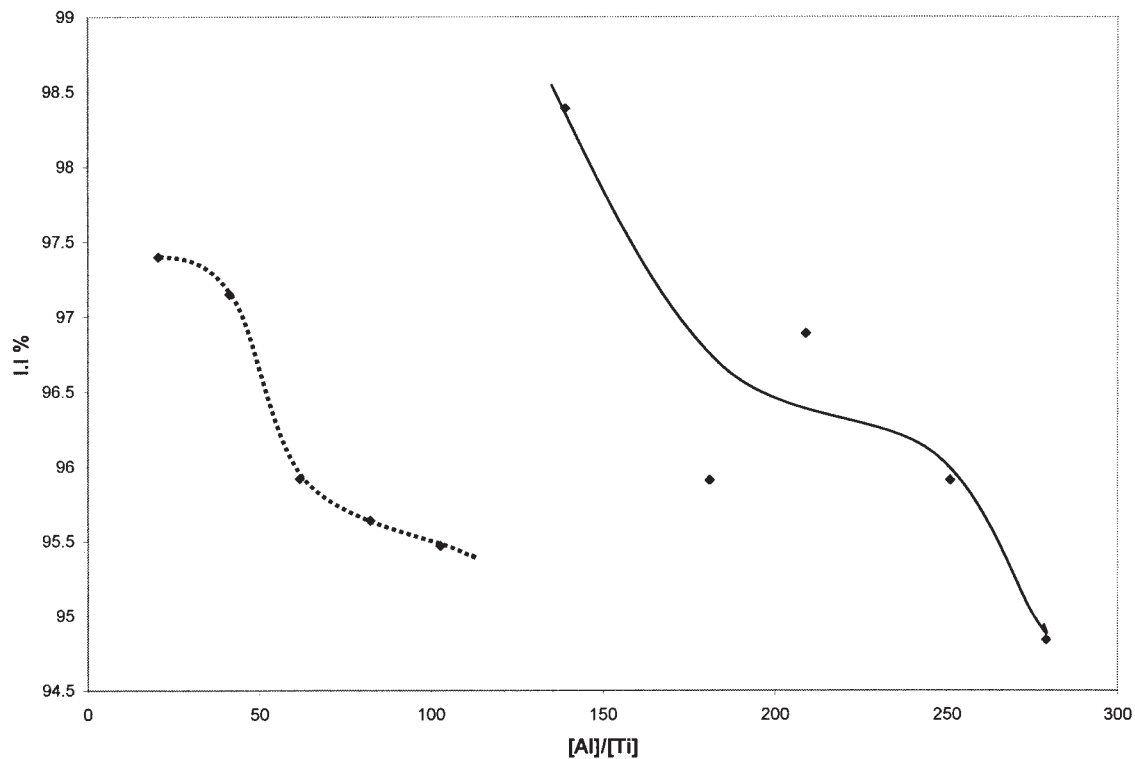


Figure 2 Effect of the $[Al]/[Ti]$ molar ratio on II (see Fig. 1 for the polymerization conditions): (\cdots) bisupported catalyst and (—) monosupported catalyst.

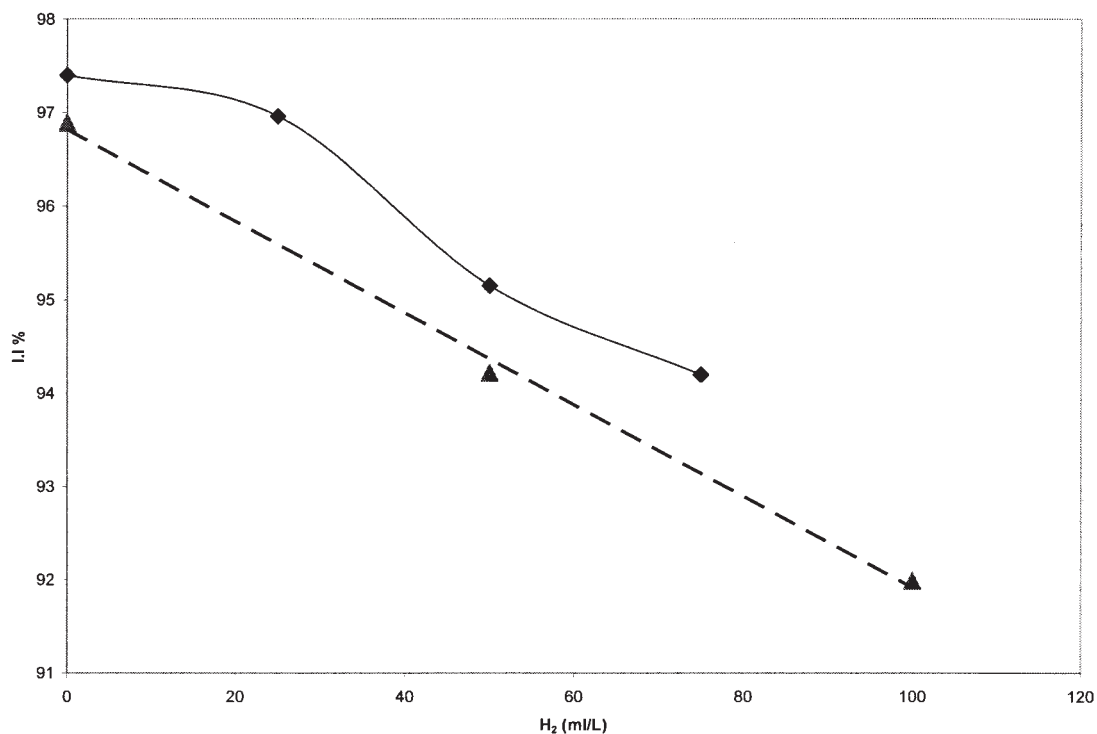


Figure 3 Plot of II versus the H₂ concentration (see Fig. 1 for the polymerization conditions): (■) bisupported catalyst ($[Ti] = 0.12$ mmol/L, $[TEA]/[DMMCHS]/[Ti] = 62:6.2:1$) and (▲) monosupported catalyst ($[Ti] = 0.18$ mmol/L, $[TEA]/[DMMCHS]/[Ti] = 209:21:1$).

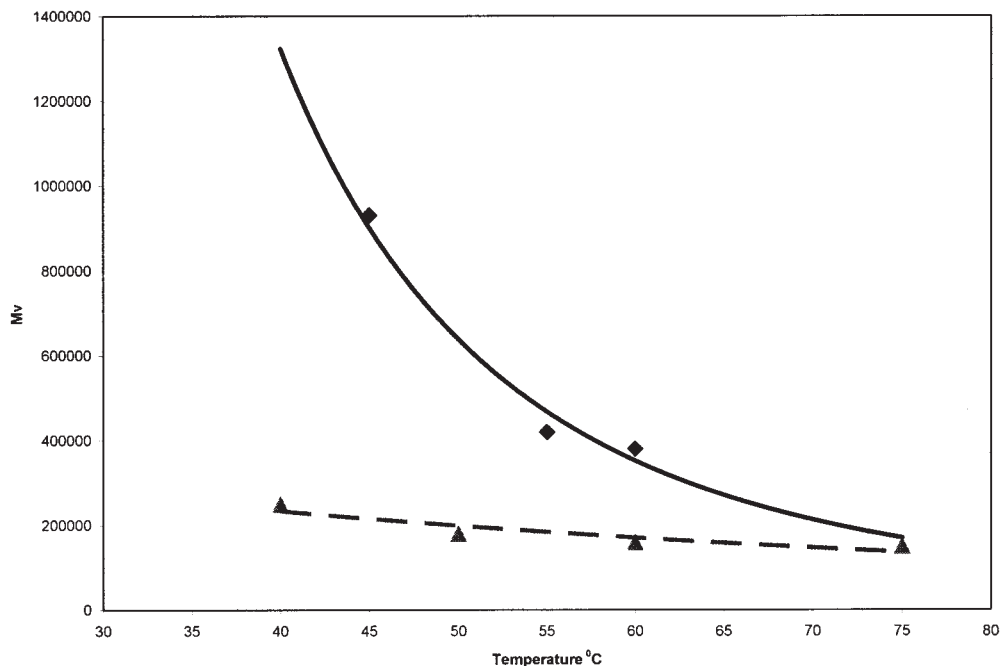


Figure 4 Effect of temperature on M_v ($[H_2] = 75$ mL/L; see Fig. 3 for the other polymerization conditions): (■) bisupported catalyst and (▲) monosupported catalyst.

ported systems showed higher activity (g of PP/mmol of Ti) and lower TEA concentrations required to obtain the highest activity. The behavior probably indicated the presence of a more stable active center in the case of the bisupported catalyst, which in the study of Weist et al.²³ showed an accelerated rate time profile for the polymerization of propylene in comparison

with a decay-type profile obtained for an $MgCl_2$ -supported catalyst.

The isotacticity index (II) of the polymer decreased with increasing TEA concentration for both catalyst systems (Fig. 2). The behavior could be due to higher chain transfer to the Al compound at a higher concentration of TEA.²¹

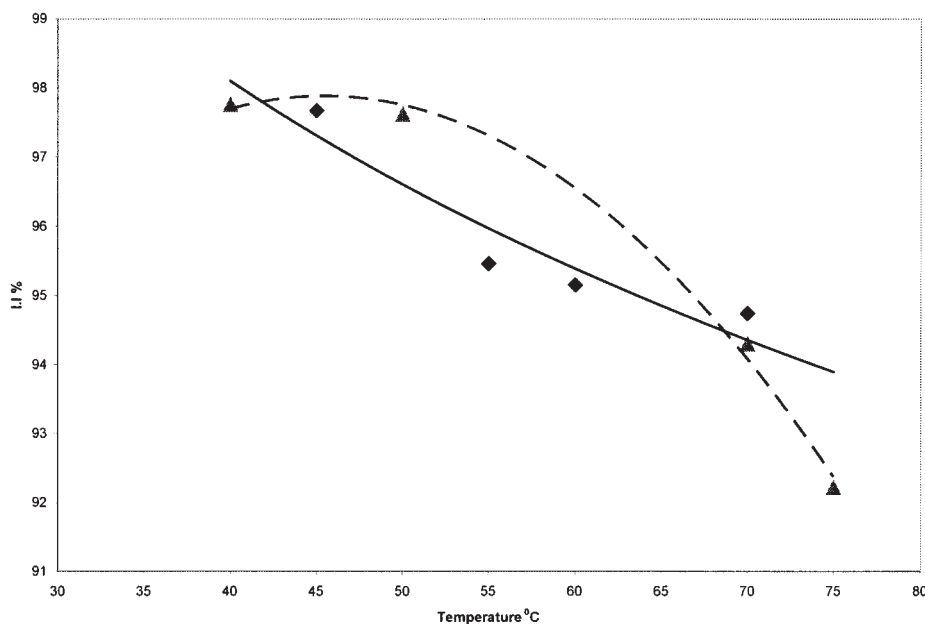


Figure 5 Effect of temperature on II ($[H_2] = 75$ mL/L; see Fig. 3 for the other polymerization conditions): (■) bisupported catalyst and (▲) monosupported catalyst.

TABLE II
Effect of Monomer Pressure on Yield of PP

	Monomer pressure (1.01×10^{-5}) (Pa)					
	2	3	4	5	6	8
Mono supported catalyst yield (g of PP/mmol of Ti)	137.7	193.6	404.1	—	508.8	852.6
Bisupported catalyst yield (g of PP/mmol of Ti)	152.3	281.8	440.5	681.2	816.0	1153.3

The polymerization conditions were the same as listed for Figure 3.

Although hydrogen was used as a chain-transfer agent, it caused an increase in the activity of the catalyst systems.^{20,21} The addition of H₂ to 100 mL/L reduced II of the polymer from about 97 to 92% (Fig. 3). The effect could be due to easy transfer of the polymer growing chain to H₂, particularly at high concentrations. The shorter the polymer chain was, the more it dissolved in boiling *n*-heptane, which was used in an extraction method to determine II.²⁴

The influence of temperatures of 40–75°C on the viscosity-average molecular weight (M_v) and II of the obtained polymer was studied (Figs. 4 and 5). In the case of PP obtained with the bisupported catalyst, M_v was higher over the whole range of temperatures studied. M_v decreased sharply with increasing polymerization temperature. II of the polymer decreased at higher temperatures. The effect of the polymerization temperature on II of PP obtained with the monosup-

ported catalyst was higher than that of the polymer obtained with the bisupported one, whereas an inverse behavior was obtained for the influence of temperature on M_v of the obtained polymer.

The lower M_v and II values of PP obtained at higher temperatures could be due to an increasing rate of chain transfer at higher temperatures.

The monomer pressure is one of the key factors that has a significant effect on the polymerization behavior and characteristics of polymers obtained with Ziegler–Natta systems. A sharp increase in the productivity of Ziegler–Natta catalysts has been reported with increasing monomer pressure.^{25–27} Table II shows the effect of a monomer pressure of $0.2–0.8 \times 10^6$ Pa on the yield of the obtained polymer. The increase in the productivity of the catalysts could be due to the higher concentration of the monomer close to catalytic active centers at higher monomer pressures and also possible fragmentation of

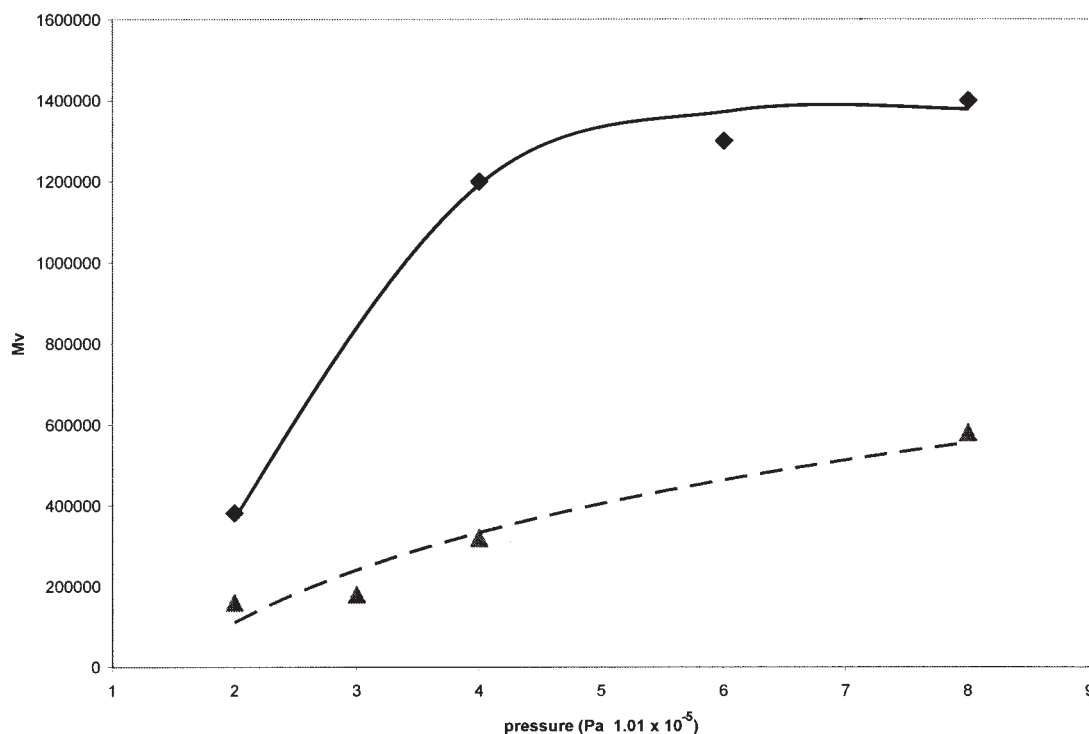


Figure 6 Effect of monomer pressure on M_v of PP (see Fig. 3 for the polymerization conditions): (\blacklozenge) bisupported catalyst and (\blacktriangle) monosupported catalyst.

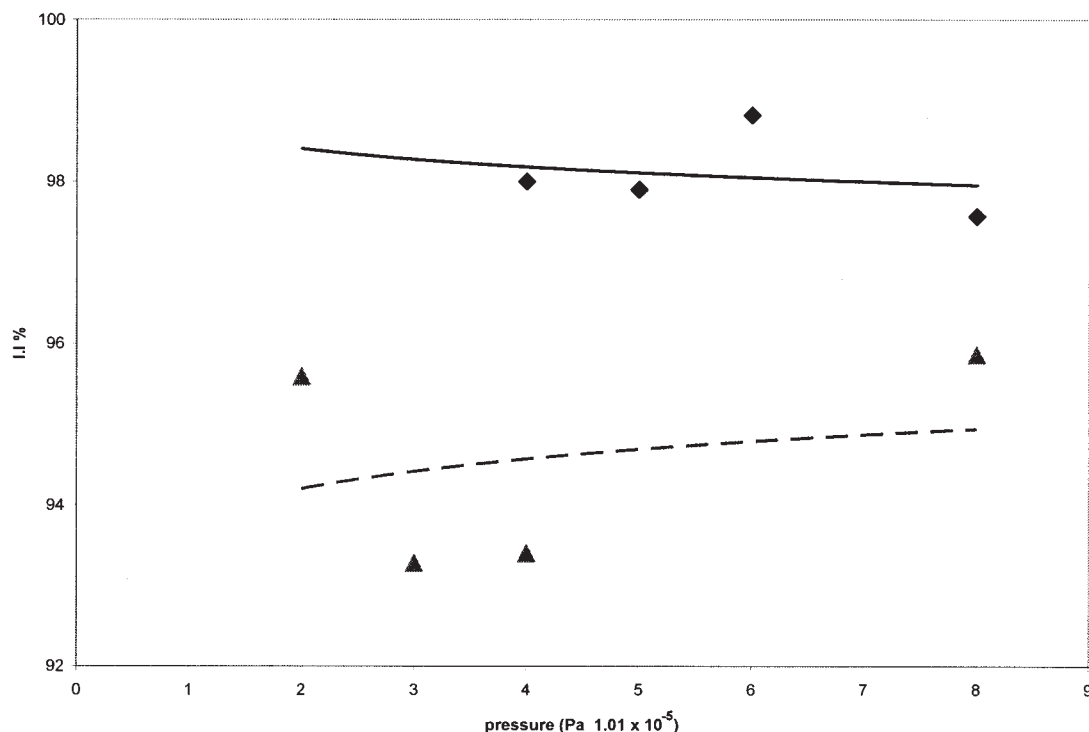


Figure 7 Effect of monomer pressure on II of PP (see Fig. 3 for the polymerization conditions): (■) bisupported catalyst and (▲) monosupported catalyst.

the catalyst particles at higher pressures.^{25–27} The bisupported catalyst system showed higher productivity in the whole range of monomer pressures studied. The behavior indicated more active centers or more activity of the active center present in the case of the bisupported systems. Figures 6 and 7 show the effects of the monomer pressure on M_v and II, respectively. For both of the studied systems, M_v increased with increasing pressure. However, II was not so much affected by the monomer pressure. Higher M_v values obtained at high pressures indicated an increasing rate of propagation in comparison with the chain-transfer reaction rate at higher pressures. The result was expected because of the higher concentration of the monomer close to the active centers in comparison with the chain-transfer agent at high monomer pressures.

CONCLUSIONS

1. Both the bisupported and monosupported catalysts showed high activity and high II values (>96%) for the polymerization of propylene.
2. The bisupported catalyst containing SiO_2 produced a catalyst with higher activity, higher surface area, and higher Ti loads.
3. The optimum activity was obtained at lower TEA concentrations for the bisupported catalyst.
4. Higher H_2 and TEA concentrations and temperatures reduced II and M_p of the obtained polymer.

5. Increasing the monomer pressure from 2.02×10^5 to 0.8×10^6 Pa increased the productivity of the catalysts sharply, increased M_v , and did not affect II much.
6. The activity of the bisupported catalyst was higher over the whole monomer pressure range studied.
7. Both M_v and II were higher for the polymer obtained with the bisupported catalyst.

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