

# Propene Polymerization with MgCl<sub>2</sub>-Supported TiCl<sub>4</sub>/Dioctylphthalate Catalyst. I. Catalyst Behavior

CHUN B. YANG and CHENG C. HSU\*

Department of Chemical Engineering, Queen's University, Kingston, Ontario K7L 3N6, Canada

## SYNOPSIS

Slurry polymerization of propene using MgCl<sub>2</sub>-supported TiCl<sub>4</sub>/dioctylphthalate catalysts were carried out in a semibatch reactor at a constant pressure to examine the effects of polymerization conditions on catalyst activity and polymer isotacticity. The catalysts were prepared at 80, 90, and 105°C, which gave different compositions of chemical complexes associated with the diester. Five alkyl aluminums (triethyl, triisobutyl, tri-*n*-hexyl, tri-*n*-octyl, and isoprenyl) were studied as cocatalysts. Among these, triethyl aluminum was found to be most effective for the catalysts prepared at 80 and 95°C, and tri-*n*-hexyl aluminum for the catalyst prepared at 105°C. Dimethoxydiphenyl silane and 2,2,6,6-tetramethyl piperidine were employed to study their effects as an external Lewis base for the catalyst prepared at 105°C. In both cases, a small amount of either base resulted in significant increase in activity and isotacticity, which can be attributed to the high level of phthaloyl chloride complex in the catalyst. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

The stereospecificity of MgCl<sub>2</sub>-supported Ziegler-Natta catalyst for propene polymerization can be greatly enhanced by using a proper combination of internal and external Lewis bases. Commonly used Lewis bases are aromatic mono- and diester. The former has been a subject of a longstanding interest among researchers.<sup>1</sup> The aromatic diester, on the other hand, has not been a subject of intense research in recent years.<sup>2-6</sup> Most of the studies have focused on elucidating the role of the base.<sup>2,7-8</sup> Only a few investigations have paid attention to how the performance of aromatic diester-containing catalysts were affected by polymerization conditions.<sup>2,6</sup>

The catalyst with diester as the internal base, in general, produces polypropene (PP) of very high isotactic index. However, the most favorable polymerization conditions for isotacticity do not coincide with those for catalyst activity. Therefore, for the effective use of such a catalyst it is important to

study how the catalyst activity and polymer isotacticity are affected by polymerization conditions.

This paper presents the performance of a MgCl<sub>2</sub>-supported TiCl<sub>4</sub> catalyst with dioctylphthalate (DOP) as an internal base in propene polymerization under different polymerization conditions. The conditions studied include different external Lewis bases, cocatalysts, cocatalyst/catalyst ratios, and polymerization temperatures.

In our previous studies,<sup>9,10</sup> infrared (IR) spectroscopic analysis of aromatic diester-containing catalysts revealed that different chemical complexes involving Lewis bases were formed on the catalyst surface. One of the complexes, phthaloyl dichloride (POC), was found to have distinct effects on catalyst activity and polymer isotacticity. The amount of POC apparently depended on the conditions under which the catalyst was prepared.

As to the external Lewis bases, three types have been known to be effective in enhancing isotacticity without seriously affecting the catalyst activity: (1) aromatic esters, such as ethyl benzoate (EB); (2) alkoxy silanes, such as phenyltriethoxy silane (PTES); and (3) sterically hindered amines, such as 2,2,6,6-tetramethyl piperidine (TMPIP). Types (2) and (3), however, have been shown to work better for the cat-

\* To whom all correspondence should be addressed.

alysts with aromatic diester as an internal Lewis base.<sup>5,6</sup> Noristi et al.<sup>11,12</sup> have shown that when an external base is employed during polymerization with a catalyst containing an internal base, a progressive decrease of the internal base occurs along with the incorporation of increasing amounts of external base onto the catalyst. The superior performance of the diester/aromatic silane donor pairs as internal and external bases was attributed to the higher incorporation of aromatic silane onto the catalyst, compared to the aromatic monoester.

We also included TMPIP and dimethoxydiphenyl silane (DMDPS) as external bases to investigate their effects on polymerization with a catalyst containing a relatively high content of POC complexes. Polymerizations were conducted at low base concentrations to better appreciate the probable stereoselective effects.

## EXPERIMENTAL

### Materials

Analytical grade *n*-heptane was obtained from BDH (VWR, London, Ontario) and dried over a 4-Å molecular sieve. TMPIP, DOP, triethyl aluminum (TEA), triisobutyl aluminum (TIBA), and TiCl<sub>4</sub> were purchased from Aldrich (Milwaukee, WI) and used as received. Anhydrous MgCl<sub>2</sub> from Aldrich was dried by successive heating to 135°C with stirring under a steady stream of dry nitrogen for 48 h and then to 200°C for another 72 h. The dryness of the treated MgCl<sub>2</sub> was checked by IR. No noticeable peak in the  $\nu(\text{OH})$  region of the spectrum was observed.

DMDPS from Tokyo Kasei (Tokyo) was used as received. Tri-*n*-hexyl aluminum (THA), tri-*n*-octyl aluminum (TOA) and isoprenyl aluminum (IPRA) were obtained from Akzo Chemicals (Chicago, IL). Propene of polymerization grade was supplied by Union Carbide, Linde Division (Belleville, Ontario), and dried by passing through columns containing drierite and a 4 Å molecular sieve.

### Catalyst Preparation

Fifteen grams of MgCl<sub>2</sub> was mixed with 1.12 g of DOP to make a molar ratio of DOP/MgCl<sub>2</sub> equal to 0.075. The mixture was ground for 120 h at room temperature in a porcelain jar one-quarter to one-third filled with burundum grinding cylinders. Four grams of the ground solids were refluxed with TiCl<sub>4</sub> (8 mL) for 2 h at a prescribed temperature. After refluxing, the slurry was filtered hot and washed with

50 mL of heptane five times at 80–95°C. The resulting catalyst was dried under a dry nitrogen atmosphere for 2 h and then under vacuum for another 30 min at room temperature. The catalyst powders were stored under a nitrogen atmosphere in a glove box. All glassware was dried at 130°C under vacuum. The assembly of glassware and the catalyst synthesis operation were carried out under a nitrogen atmosphere inside the glove box (AE-543; Vacuum Atmosphere Ltd. VML, Burlington, Ontario), in which the moisture and oxygen contents were maintained below 10 ppm.

The wt % of titanium in the catalyst was determined by a colorimetric method. A known mass of catalyst powder was dissolved in 10 mL of concentrated sulphuric acid, to which 10 mL of 3% H<sub>2</sub>O<sub>2</sub> was added. The visible ultraviolet (UV-vis) absorbance was then measured on a Philips 8700 spectrophotometer. The wt % of titanium was calculated from a calibration curve derived from absorbance measurements of standard Ti solutions.

### Polymerization

Propene polymerization was carried out in a 250 mL stainless steel autoclave (Autoclave Engineers Inc., Erie, PA, USA). The reactor was operated in a semibatch mode where the monomer was introduced continuously to maintain a constant pressure without removing polymer products.

The reactor was heated with hot air gun and assembled while still hot. It was further heated overnight under vacuum and then thoroughly purged with dry nitrogen before dry *n*-heptane was drawn into the reactor for polymerization. The temperature control was set in and monomer was introduced. Once the temperature stabilized and the solvent was saturated with monomer, a known volume of aluminum alkyl solution, and an external Lewis base when an external base was employed, were added. Aluminum alkyl solution was injected first to scavenge any residual moisture or oxygen left in the system. The catalyst was finally introduced with an aid of catalyst cartridge to start polymerization. The monomer flow rate was monitored by an electronic mass flow meter and recorded as a function of time. The polymerization was stopped by the addition of a 1% hydrochloric acid solution of methanol. Then the reactor contents were poured into a large volume of the acidified methanol and stirred for at least 12 h. The polymer was filtered, washed with methanol, and dried to a constant weight.

The catalyst activity was calculated as the weight of PP produced per gram of titanium in the catalyst per hour.

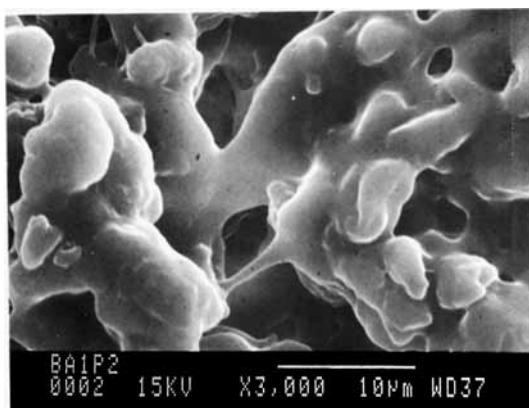
The isotactic index (II) of PP was determined by extracting PP in a Soxhlet extractor with boiling heptane for 12 h, and is shown as a wt % of polymer insoluble in the boiling heptane. The reproducibility of the II was estimated by replications to be  $\pm 1.1\%$  standard deviation.

## RESULTS AND DISCUSSION

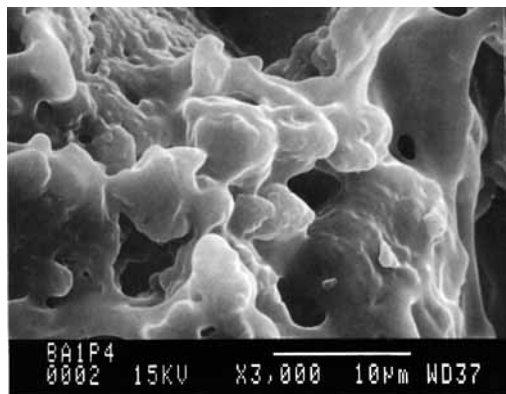
In our previous investigations<sup>10,13</sup> we confirmed by IR spectroscopy the formation of three chemical complexes ( $\text{MgCl}_2/\text{DOP}$ ,  $\text{MgCl}_2/\text{POC}$ , and  $\text{TiCl}_4/\text{DOP}$ ) on the  $\text{TiCl}_4/\text{DOP}$  catalyst supported on  $\text{MgCl}_2$  as prepared by milling or by precipitation from a ROH (R = alkyl) solution of  $\text{MgCl}_2$ . POC was formed by the reaction between  $\text{TiCl}_4$  and DOP. The amounts of the three complexes were found to be dependent on the refluxing temperature, the temperature at which  $\text{TiCl}_4$  was treated during catalyst preparation. Three catalysts designated as catalyst A, B, and C were prepared at  $80^\circ\text{C}$ ,  $95^\circ\text{C}$ , and  $105^\circ\text{C}$ , respectively. The ratio of POC/DOP increased from 0.57 at a refluxing temperature of  $80^\circ\text{C}$  to 1.99 at  $105^\circ\text{C}$ . The absolute and/or relative amount of POC and DOP complexes to  $\text{MgCl}_2$  was found to have a significant influence on the catalyst activity and polymer isotacticity.

### Polymer Morphology

Scanning electron photomicrographs (SEM) of the polymer produced by catalyst A, prepared at  $80^\circ\text{C}$ , were taken using an acceleration voltage of 2 to 20 kV. The polymer samples were deposited on SEM stub and sputter-coated with carbon to reduce



**Figure 1** SEM micrograph ( $\times 3,000$ ) of PP obtained with catalyst A-TEA system. Polymerization conditions: temperature,  $50^\circ\text{C}$ ;  $[\text{Ti}] = 0.12 \text{ mmol/L}$ ;  $\text{Al/Ti} = 50$ .



**Figure 2** SEM micrograph ( $\times 3,000$ ) of PP obtained with catalyst A-TOA system. Polymerization conditions were the same as in Figure 1.

charging effects. The morphologies of PP using two different cocatalysts are presented in Figures 1 and 2, which show polymer particles in the form of interconnected globular aggregates. It is believed that the catalyst particles disintegrate into nascent particles during polymerization,<sup>14</sup> and that each contains one or more catalyst crystallites.<sup>15</sup> In general, the polymer particle morphology can be considered replicated from that of catalyst particles, a generally observed occurrence in heterogeneous Ziegler-Natta polymerizations.<sup>16</sup> The fibrous structure is believed to be formed as the polymer particles grow and also as the result of shearing forces created by vigorous agitation. Similar particle morphologies as shown in Figures 1 and 2 were obtained for polymers produced by catalysts prepared at other temperatures.

### Catalyst Activity and Stereospecificity

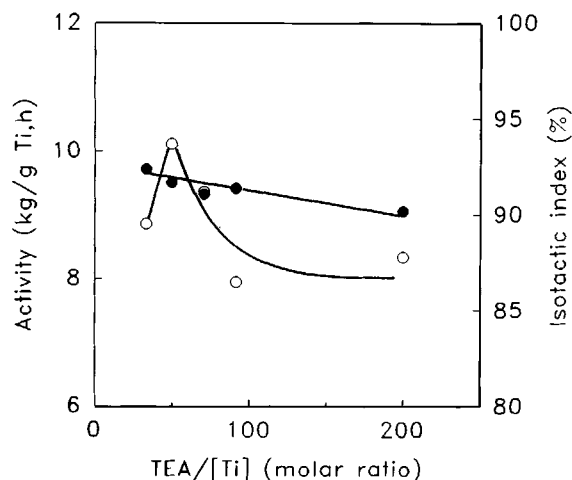
Although a  $\text{MgCl}_2$ -supported catalyst yields PP with a very high content of isotactic polymer under proper polymerization conditions, the effects of polymerization conditions on activity and isotactic index are rather complicated. Often the most favorable conditions for activity and those for stereospecificity do not coincide; and when an external base is used to enhance stereospecificity, the electron donor usually has an adverse effect on activity. To examine this in detail for the  $\text{MgCl}_2/\text{DOP}/\text{TiCl}_4$ -alkyl aluminum catalyst system, polymerizations were carried out under various polymerization conditions: different types of alkyl aluminum as cocatalyst,  $\text{Al/Ti}$  ratios, polymerization temperatures, and concentrations of TMPIP or DMDPS added as an external base.

### Alkyl Aluminums

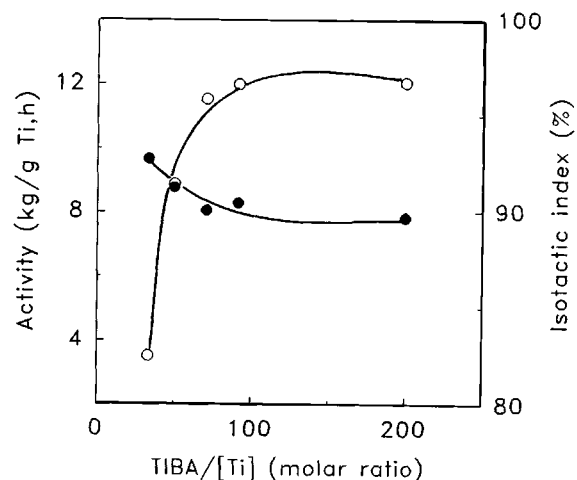
Trialkyl aluminums are the most commonly used cocatalysts for  $\text{MgCl}_2$ -supported catalysts, whereas the halogen-containing analogue gives rather low catalyst activity. Among various trialkyl aluminums, it was found by previous investigators<sup>17</sup> that an increase in the size of the alkyl groups (from ethyl to octyl, for example) induced an increase in catalyst activity. The observed influence of cocatalyst was attributed to a combined effect of several simultaneous reactions, such as alkylation and reduction of Ti, extraction of internal base, and catalyst modification.<sup>18</sup>

In our previous publication,<sup>13</sup> the effectiveness of four different cocatalysts—TEA, TIBA, THA, and TOA—was discussed. Their effects on catalyst performance depended somewhat on the refluxing temperature. For catalysts A and B, prepared at 80°C and 95°C, respectively, both catalyst activity and polymer isotacticity decreased in the order TEA > TIBA > THA > TOA. For catalyst C, which was prepared at 105°C, THA gave the highest activity, but the isotacticity followed the same order as with the other two catalysts. This unusual trend could be the result of a high level of POC complex in catalyst C. The effects of various trialkyl aluminums on the activity obtained with our catalysts contradict those of the previous authors.<sup>17</sup> This could be due to the difference in catalyst and monomer type.

The catalyst activity and stereospecificity of polymer are also influenced by the concentration of alkyl aluminums. Figures 3 and 4 depict the dependencies of activity and isotactic index on the Al/Ti



**Figure 3** Effect of TEA/Ti ratio on activity and isotactic index for catalyst A (○, activity; ●, isotactic index). Polymerization conditions:  $[\text{Ti}] = 0.12$  mmol/L; polymerization temperature = 50°C; Al/Ti = 50; propene partial pressure = 118 kpa; polymerization time = 1 h.

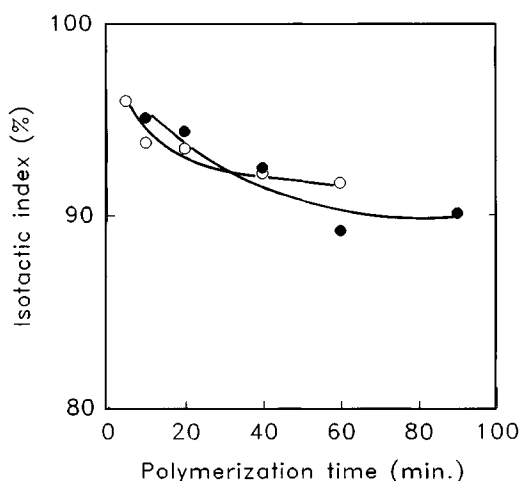


**Figure 4** Effect of TIBA/Ti ratio on activity and isotactic index for catalyst A (○, activity; ●, isotactic index). Polymerization conditions were the same as in Figure 3.

ratio. For catalyst A with TEA as cocatalyst, the maximum activity is at around TEA/Ti = 50, while the isotactic index decreases slightly with an increasing TEA/Ti ratio (Fig. 3). On the other hand, with TIBA as a cocatalyst, the activity increases with the TIBA/Ti ratio up to TIBA/Ti = 70 and then remains unchanged, whereas the isotactic index follows a similar trend as that of TEA (Fig. 4).

An optimum activity is generally observed for supported Ziegler–Natta catalysts with respect to the molar ratio of Al/Ti within the range 10 to 30.<sup>19</sup> Keii et al.<sup>20</sup> and Burfield et al.<sup>21</sup> used the competitive adsorption argument to explain the optimum activity, while Dumas and Hsu<sup>22</sup> demonstrated, based on a multiple active site model, that the optimum activity may occur when sites of widely different activities also have different rates of deactivation. Overall, the increase of activity in the low range of TEA concentration might be due to the progressive activation of potential sites by TEA,<sup>23</sup> whereas the decrease in activity at high concentrations of TEA might be ascribed to the overreduction of titanium.<sup>24</sup> Thus different Al/Ti ratios lead to the different distributions of site activities.

Soga et al.<sup>2</sup> reported only a slight decrease or no change in isotacticity with respect to Al/Ti ratio for a  $\text{MgCl}_2$ -supported catalyst containing di-*n*-butylphthalate as an internal base. From the fact that the internal base complexed with catalyst can be extracted by alkyl aluminum,<sup>1</sup> they attributed the small change in isotacticity with changing Al/Ti ratios to the stronger complexation of diester with the Ti species and/or  $\text{MgCl}_2$ . The strong complex formation of DOP is also reflected in Figure 5, in



**Figure 5** Change of isotactic index during polymerization for catalyst A with TEA and TOA as the cocatalyst (○, TEA; ●, TOA). Polymerization conditions were the same as in Figure 3.

which only a slight decrease of isotactic index is shown with increasing polymerization time. The figure also shows similar results between TEA and TOA.

#### Effect of Temperature

The influence of polymerization temperature on catalyst activity and isotacticity is given in Figure 6, which shows a maximum catalyst activity at around 40–50°C. Other investigators<sup>20,22,25</sup> reported the maximum activity at about 50–60°C for the MgCl<sub>2</sub>-supported TiCl<sub>4</sub> catalyst. It is believed that as temperature increases, progressive irreversible deactivation of active sites becomes dominant over the increase in propagation with temperature.<sup>20</sup> By analyzing their polymerization rate data, Dumas and Hsu<sup>26</sup> used a multisite kinetic model to demonstrate how the kinetic parameters for the propagation and deactivation reactions changed with temperature to give a maximum activity.

The isotactic index remains essentially constant up to 50°C and then decreases slightly thereafter. The decrease of isotacticity at high temperatures can be attributed to higher abstraction of the internal base by aluminum alkyl.<sup>11,12</sup> The effect of temperature on isotacticity was also explained by Barbe et al.<sup>1</sup> and Seppala et al.<sup>27</sup> on the basis of the distribution of active sites and the difference in temperature dependencies of the propagation rate constant and deactivation rate constant for isospecific and aspecific sites.

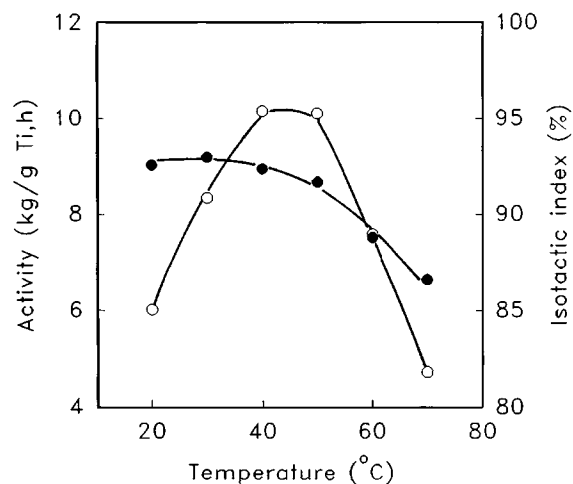
#### Effects of External Lewis Bases

Many types of Lewis base, including alcohols, esters, amines and silanes, have been employed as additives

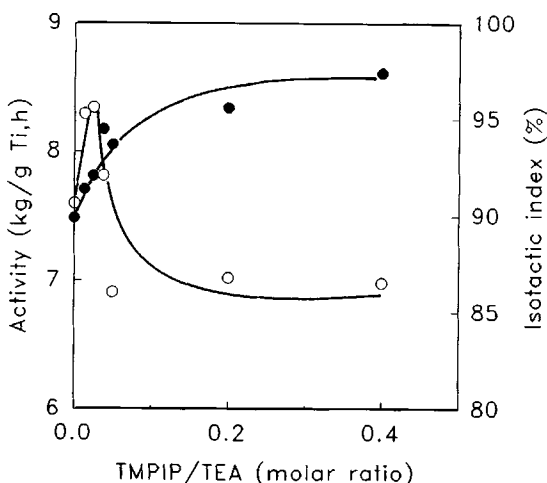
during polymerization to improve stereospecificity of MgCl<sub>2</sub>-supported catalysts in propene polymerization. However, the external Lewis base often has an adverse effect on catalyst activity. A few exceptions do exist. For example, with a MgCl<sub>2</sub>-supported TiCl<sub>4</sub> catalyst containing an aromatic diester as an internal base, the addition of alkoxy silane or hindered amine gives a polymer of high isotacticity without much depression of activity.<sup>2,5</sup>

Our previous work<sup>28</sup> also indicated that regardless of the chemical composition of the catalyst induced by different refluxing temperatures, DMDPS and TMPIP effectively improve stereospecificity with little effect on the catalyst activity. To examine more closely the roles of these external bases, we selected one of the catalysts (catalyst C) which contains a high level of POC complex to study the polymerization of propene with changing concentrations of the two external bases, DMDPS and TMPIP. As shown in Figures 7 and 8, both DMDPS and TMPIP show similar effects on activity and isotactic index. The catalyst activity increases sharply with a small amount of DMDPS or TMPIP, reaches maximum at a molar ratio of about base/TEA = 0.013–0.025, and then remains fairly constant at high base concentrations. Isotactic index, on the other hand, increases initially with base concentration and then levels off.

Using the data in Figures 7 and 8, we calculated isotactic and atactic activities and plotted them in Figures 9 and 10. The base clearly promotes isotactic activity at low concentration, but it suffers greatly with further addition of bases. The depression of isotactic activity by TMPIP at high concentration



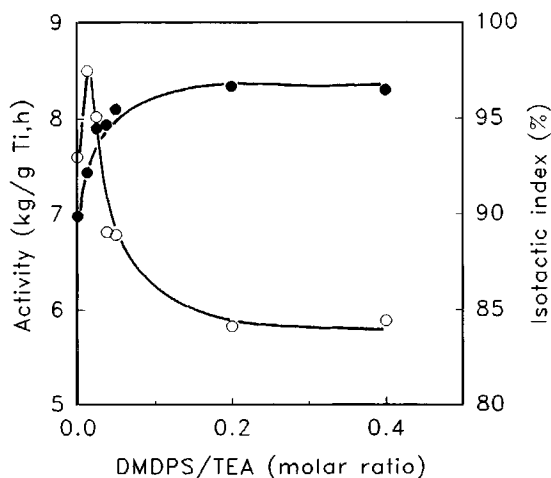
**Figure 6** Effect of polymerization temperature on activity and isotactic index for catalyst A (○, activity; ●, isotactic index). Polymerization conditions were the same as in Figure 3.



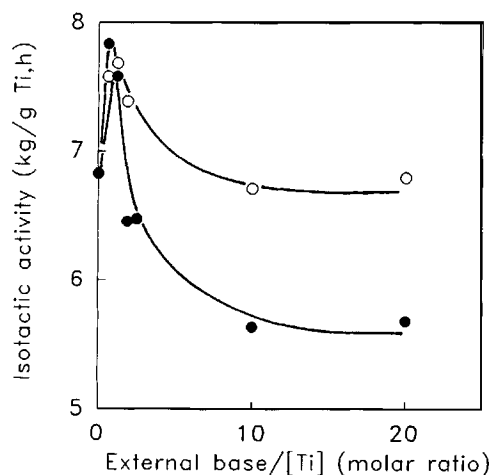
**Figure 7** Effect of TMP/IP/TEA on activity and isotactic index for catalyst C (O, activity; ●, isotactic index). Polymerization conditions were the same as in Figure 3.

is less than that by DMDPS. On the contrary, the atactic activity drops drastically with the addition of a small amount of an external base. The decrease of atactic activity levels off somewhat as the concentration of the base increases.

The increase in activity with a small amount of base (Figs. 7 and 8) can be attributed to the selective increase of the isotactic activity (Figs. 9 and 10). This increase in isotactic activity at low base concentrations has been witnessed by several other authors: Barbe et al.<sup>29</sup> with  $MgCl_2/TiCl_4-TEA/TMPIP$  or PTES catalyst systems; Dumas and Hsu<sup>22</sup> with  $MgCl_2/EB/TiCl_4-TEA/TMPIP$  catalyst systems; and Soga et al.<sup>2</sup> with  $MgCl_2/di-n-butyl\ phthalate/TiCl_4-TEA/PTES$ . In our catalyst system, the increase in isotactic activity at low concen-



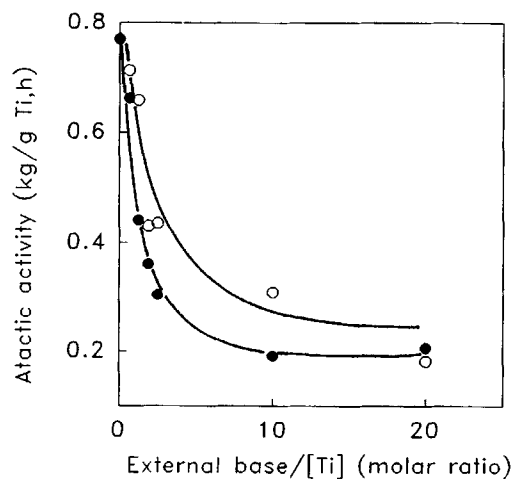
**Figure 8** Effect of DMDPS/TEA on activity and isotactic index for catalyst C (O, activity; ●, isotactic index). Polymerization conditions were the same as in Figure 3.



**Figure 9** Effect of the external base/Ti on isotactic polymer activity for catalyst C (O, TMP/IP; ●, DMDPS).

trations seems to be more pronounced than in other systems mentioned above. The high POC content in our catalyst (catalyst C) could be the reason for the difference. Perhaps the increase in POC content induced by the complexation of TEA and the external base allows the external base to incorporate more easily onto the catalyst.

Different roles of the electron donors have been suggested in stereospecific polymerizations. They include: (a) selective poisoning of nonstereospecific sites<sup>1,4,30</sup>; (b) making more sites active or increasing the propagation rate constant<sup>1,2,31,32</sup>; and/or (c) conversion of nonstereospecific sites into stereospecific sites.<sup>1,32,33,34</sup> Overall, the external base improves isotacticity by blocking aspecific sites, but the increase in total and isotactic polymer suggests that the base does much more than poisoning the atactic sites. It is possible that the base or base-aluminum



**Figure 10** Effect of the external base/Ti on atactic polymer activity for catalyst C (O, TMP/IP; ●, DMDPS).

alkyl complex transforms nonstereospecific sites into stereospecific sites, as suggested above.

## CONCLUSIONS

Based on the polymerization results obtained in this study, we can conclude that:

1. There exists an optimum activity at a TEA/Ti ratio of about 50, while the activity increased rapidly up to TIBA/Ti = 50 and leveled off beyond that ratio.
2. The optimum polymerization temperature with respect to activity is at about 40–50°C.
3. The isotactic index decreases with increasing Al/Ti ratios as well as polymerization temperatures.
4. The addition of a small amount of TMPIP or DMDPS improves isotacticity and catalyst activity.

The effects of polymerization conditions on microtacticity of isotactic polymer, molecular weight, and molecular weight distribution will be discussed in subsequent papers of this series.

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