

# Performance Improvement of $\text{MgCl}_2$ /Dioctylphthalate/ $\text{TiCl}_4$ Catalyst in Propene Polymerization by Employing External Base Pair

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## SYNOPSIS

The individual roles of three different types of external Lewis bases, namely *t*-butylmethyl ether (TBME), 2,2,6,6-tetramethyl piperidine (TMPIP), and dimethoxydiphenyl silane (DMDPS), in propene polymerization using  $\text{MgCl}_2$ /dioctylphthalate (DOP)/ $\text{TiCl}_4$  catalyst were studied. The role of TBME was found to be distinctly different from others. More active sites were believed to be activated in the presence of TBME, whereas the others seemed to play a role of converting atactic sites into isotactic ones. That difference made it possible to improve both catalyst activity and isotacticity by employing TBME together with one of the others as the external base pair. Due to the differences in the coordination strength of these bases with the catalyst, the order of addition of the two bases became important in achieving good results. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

It is well known that stereospecific polymerizations of  $\alpha$ -olefin with  $\text{MgCl}_2$ -supported Ti catalysts require the use of an appropriate pair of internal and external Lewis bases to achieve high isotacticity of polymer products.<sup>1</sup> One typical example is the pairing of an aromatic diester with an alkoxy silane in the  $\text{MgCl}_2$ -supported  $\text{TiCl}_4$  catalyst.<sup>2-5</sup>

Our IR spectroscopic investigation<sup>6</sup> of the  $\text{MgCl}_2$ -supported catalyst with dioctyl phthalate (DOP) as an internal base revealed that DOP and phthaloyl chloride (POC), a reaction product of DOP and  $\text{TiCl}_4$ , formed complexes with  $\text{MgCl}_2$  and  $\text{TiCl}_4$ . The POC complex with  $\text{MgCl}_2$  was found to have direct influence on catalyst performance in propene polymerization. Further studies indicated that when *t*-butylmethyl ether (TBME) was used as an external base, catalyst activity was enhanced but the stereospecificity remained almost unaffected.<sup>7,8</sup>

The role of the Lewis base in stereospecific polymerization of propene has been a subject of intensive research. It has been recognized that the base enhances polymer isotacticity associated with a re-

duction in activity. The increase of isotacticity has been attributed to the greater decrease of atactic polymer than that of isotactic polymer.<sup>9,10</sup> Even though there is still a lack of complete understanding on the subject, different roles of Lewis base, not necessarily mutually exclusive, have been suggested: (a) selective poisoning of nonstereospecific sites,<sup>1,5,11</sup> (b) conversion of nonstereospecific sites into stereospecific sites,<sup>1,2,12,13</sup> and (c) making more sites active or enhancing the propagation rate constant.<sup>1,13-15</sup> Thus, a right combination of internal and external bases can make the improvement of stereospecificity possible without depressing catalyst activity.

In this context, we examined the roles of three different types of external bases in propene polymerization with  $\text{MgCl}_2$ /DOP/ $\text{TiCl}_4$ -TEA catalysts and then utilized the different roles those bases play to study the possibility of improving both catalyst activity and isotacticity by employing a combination of two external bases of different types.

## RESULTS AND DISCUSSION

Three catalysts designated as A, B, and C were prepared by reacting  $\text{TiCl}_4$  with  $\text{MgCl}_2$  support at 80°C,

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95°C, and 105°C, respectively. Different activation temperatures gave different compositions of chemical complexes of DOP (internal base) and POC with MgCl<sub>2</sub> and TiCl<sub>4</sub> in the catalyst.<sup>8</sup> As the activation temperature increased from 80 to 105°C, the ratios of POC to DOP in catalysts A, B, and C were found to be 0.566 : 0.794:1.99, respectively.

Table I gives the polymerization results using these catalysts with or without external base. Three different types of Lewis bases, namely TBME, TMPIP, and DMDPS, were employed separately as the external base. The catalyst B showed the highest activity among three catalysts with or without TBME. The use of TBME as an external base increased the activity by about 2.5–3.3 kg PP/gTi/h for all three catalysts. The isotactic index (I.I.) of the polymer product as a whole and the isotactic triad, [mm] of the isotactic polymer portion remained largely unchanged with or without TBME. Therefore, the amounts of isotactic and atactic polymers increased for all three catalysts with the use of TBME. The results seem to suggest that the presence of TBME increases the populations of both atactic and isotactic sites.

When TMPIP or DMDPS was used, the catalyst activity fell slightly with a significant enhancement of stereospecificity. The addition of TMPIP or DMDPS also strengthened stereospecific insertion of monomer as shown in the enhancement of [mm] in the isotactic polymer. For MgCl<sub>2</sub>-supported TiCl<sub>4</sub> catalysts, many authors<sup>2,17</sup> proposed the coexistence of two different isospecific sites in the presence of

an external base: (1) "low" isospecific sites featuring a Cl vacancy that produce less isotactic polymer; and (2) "high" isospecific sites with Lewis base attached that give highly isotactic polymer. Thus, it is reasonable to speculate that in this work the increase in [mm] in the isotactic portion of polymer when TMPIP or DMDPS was added, is the result of the conversion of atactic sites to "high" isotactic ones.

The above arguments suggest that the role of TBME is different from that of either DMDPS or TMPIP. To examine this difference, propene polymerizations were carried out using dual external bases, TBME paired with TMPIP or DMDPS. First, the two bases were added together before the start of polymerization. The results are given in Table II. Interestingly, as compared with the data for adding TMPIP or DMDPS alone, there are no appreciable changes in activity and I.I. The effect of TMPIP or DMDPS seems to overshadow the influence of TBME on polymerization, as we have seen when TBME was added alone. Another interesting point to note is that isotactic triads, [mm] of the isotactic polymers produced by all three catalysts decreased somewhat, as compared to those where TMPIP or DMDPS was added alone. In fact, they were almost the averages between the isotactic triads of isotactic polymers produced in the presence of TBME and of TMPIP or DMDPS. Because the use of TBME alone did not change the isotactic triads of the isotactic polymers, this may suggest that some of the stereospecific sites activated by TMPIP or DMDPS

**Table I Results of Propene Polymerizations of Catalyst A, B and C Using Different External Bases. Polymerization Conditions: Monomer Partial Pressure, 118 kPa; [Ti], 0.12 mmol/L; Molar Ratio of TEA/Ti, 50; Polymerization Temperature, 50°C; Duration of Polymerization, 1 h.**

Catalyst	External Base <sup>a</sup>	E.B./TEA (molar ratio)	Activity (kg PP/g Ti/h)	I.I. <sup>b</sup> (wt %)	[mm] <sup>c</sup> (mol %)
A	—	—	9.6	91.7	93.0
	TBME	0.029	12.9	91.3	93.7
	TMPIP	0.05	9.2	96.0	96.5
	DMDPS	0.05	8.4	96.4	97.4
B	—	—	11.0	91.2	92.6
	TBME	0.029	13.5	91.4	91.8
	TMPIP	0.05	10.3	95.7	95.0
	DMDPS	0.05	7.4	95.6	97.2
C	—	—	7.6	89.9	92.1
	TBME	0.05	10.1	88.7	92.5
	TMPIP	0.05	6.9	93.7	94.6
	DMDPS	0.05	6.8	95.5	95.7

<sup>a</sup> TBME = t-butylmethyl ether; TMPIP = 2,2,6,6-tetramethylpiperidine; DMDPS = dimethoxydiphenyl silane.

<sup>b</sup> I.I. = isotactic index. I.I. was measured as the weight percent of polymer insoluble in boiling heptane.

<sup>c</sup> [mm] = isotactic triad of isotactic polymer estimated from IR spectrum.

**Table II** Effects of External Base Pairs on Propene Polymerization. Polymerization Conditions Were the Same as in Table 1. Two External Bases Were Added Together Before the Polymerization Started (TMPIP or DMDPS/TEA = 0.05).

Catalyst	External Base Pair	TBME/TEA (molar ratio)	Activity (kg PP/g Ti/h)	I.I. <sup>a</sup> (wt %)	[mm] <sup>b</sup> (mol%)
A	TBME, TMPIP	0.029	9.6	95.7	94.3
	TBME, DMDPS	0.029	7.6	97.2	95.6
B	TBME, TMPIP	0.029	10.3	97.2	93.9
	TBME, DMDPS	0.029	7.6	96.2	95.8
C	TBME, TMPIP	0.05	9.1	93.0	93.9
	TBME, DMDPS	0.05	5.5	96.4	94.7

<sup>a</sup> I.I. = isotactic index measured as the weight percent of polymer insoluble in boiling heptane.

<sup>b</sup> [mm] = isotactic triad of isotactic polymer estimated from IR spectrum.

were replaced by TBME or TBME/TEA complex. One may also argue that TMPIP or DMDPS (or their TEA complexes) do not interact with TBME, but rather directly with active sites.

If the latter argument is true, it might be possible to improve both activity and isotacticity by adding the two external bases separately. Table III presents the results of propene polymerizations where TBME was added before polymerization started, followed by the addition of TMPIP or DMDPS with a 5- or 10-min delay. By comparing the activities and isotactic indices in Table III with those results where TMPIP or DMDPS was added alone (see Table I), it can be seen that all three catalysts showed a significant improvement in activity, although the isotactic indices remained unchanged.

The result is in agreement with that of Ohnishi et al.<sup>16</sup> Their data showed that the effect of aromatic

ester as an external base on catalyst isotacticity was not compromised by the presence of TBME, while the use of TBME and aromatic ester together increased catalyst activity.

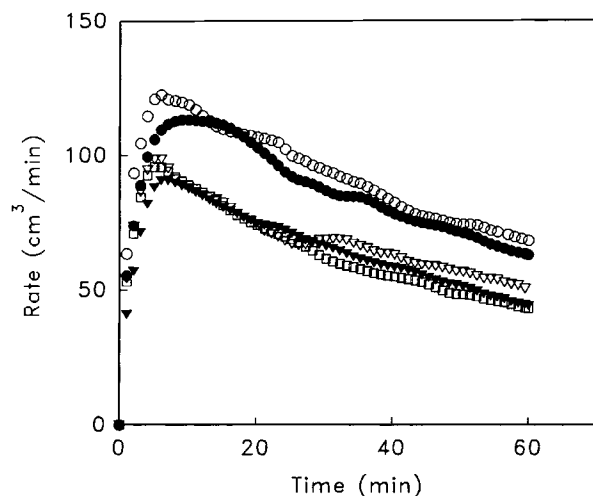
Figure 1 shows a comparison of kinetic behaviors of catalyst A under different modes of TBME and TMPIP additions. Figure 2 shows the corresponding results involving TBME and DMDPS. The results lead to the same conclusion as discussed previously, that more sites were activated in the presence of TBME. First, the maximum polymerization rate, which can be considered as the point at which all active sites are being activated before any deactivation occurs, is much higher for the TBME addition. This suggests that there are either more active sites activated or sites being more active. However, the two kinetic curves follow a closely parallel pattern, which is an indication of the former, because,

**Table III** Effects of External Base Pairs on Propene Polymerization. Polymerization Conditions Were the Same as in Table 1. Two External Bases Were Added Separately With a Time Interval; TBME Was Added First Before Polymerization; (TMPIP or DMDPS/TEA = 0.05).

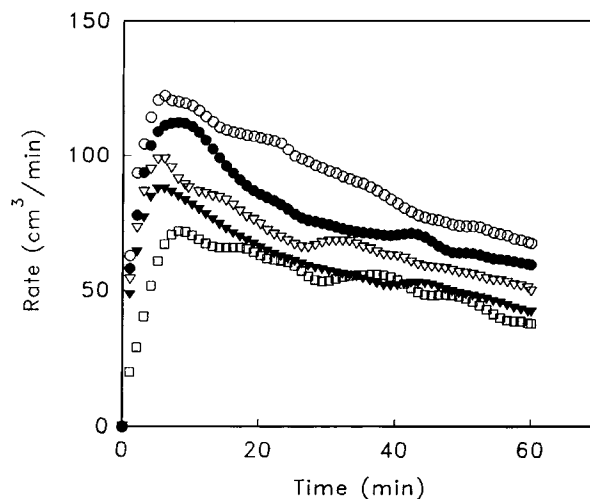
Catalyst	External Base Pair	TBME/TEA (molar ratio)	Time of TMPIP or DMDPS Addition (min)	Activity (kg PP/g Ti/h)	I.I. <sup>a</sup> (wt %)	[mm] <sup>b</sup> (mol %)
A	TBME, TMPIP	0.029	5	12.1	95.1	94.7
	TBME, TMPIP	0.029	10	11.4	94.7	94.5
	TBME, DMDPS	0.029	10	11.0	95.2	95.5
B	TBME, TMPIP	0.029	5	13.1	94.5	94.9
	TBME, TMPIP	0.029	10	12.5	94.1	94.0
	TBME, DMDPS	0.029	10	10.8	94.3	94.9
C	TBME, TMPIP	0.05	5	9.3	92.7	93.6
	TBME, TMPIP	0.05	10	9.2	92.0	93.6
	TBME, DMDPS	0.05	10	7.4	92.5	95.0

<sup>a</sup> I.I. = isotactic index measured as the weight percent of polymer insoluble in boiling heptane.

<sup>b</sup> [mm] = isotactic triad of isotactic polymer estimated from IR Spectrum.



**Figure 1** Kinetic curves of propene polymerization with catalyst A with different addition modes of the external bases. Polymerization conditions were the same as given in Table I: ( $\nabla$ ) without base; ( $\circ$ ) TBME (TBME/TEA = 0.029); ( $\square$ ) TMPIP (TMPIP/TEA = 0.05); ( $\blacktriangledown$ ) TBME+TMPIP (TBME/TEA = 0.029, TMPIP/TEA = 0.05), where both bases were added together before the start of polymerization; ( $\bullet$ ) TBME+TMPIP (TBME/TEA = 0.029, TMPIP/TEA = 0.05), where TMPIP was added 5 min after the start of polymerization.



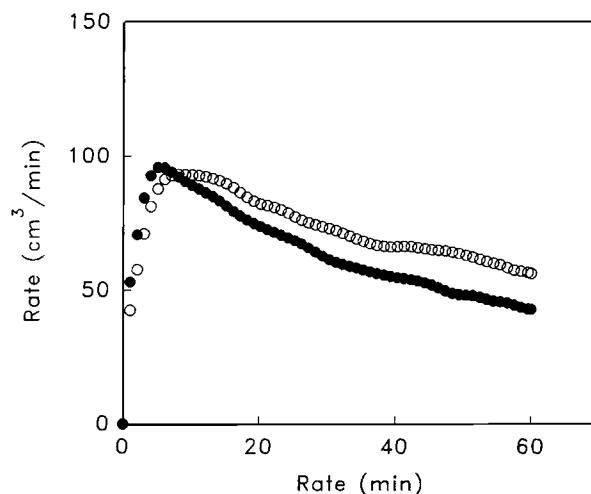
**Figure 2** Kinetic curves of propene polymerization with catalyst A with different addition modes of the external bases. Polymerization conditions were the same as in Table I: ( $\nabla$ ) without base; ( $\circ$ ) TBME (TBME/TEA = 0.029); ( $\blacktriangledown$ ) DMDPS (DMDPS/TEA = 0.05); ( $\square$ ) TBME+DMDPS (TBME/TEA = 0.029, DMDPS/TEA = 0.05) where both bases were added together before the start of polymerization; ( $\bullet$ ) TBME+DMDPS (TBME/TEA = 0.029, DMDPS/TEA = 0.05) where DMDPS was added 10 min after the start of polymerization.

if the latter were true, the kinetic profile would follow a different pattern due to the fact that sites of higher activity usually deactivate faster.<sup>18-20</sup>

Figures 1 and 2 also show the kinetic profiles for the addition of TBME with TMPIP (or DMDPS) together. TMPIP or DMDPS was added 5 or 10 min after the start of polymerization. Clearly, polymerization rates were higher when TBME was added first. The subsequent addition of the second base did not alter the course of polymerization. Therefore, it might be reasonable to believe that the coordination of the potential sites with TMPIP or DMDPS (or their TEA complex) appears to be stronger than that with TBME or TBME/TEA. Once the potential sites are coordinated with TMPIP or DMDPS, the activation of those sites by TBME becomes less effective.

To further examine this point, we performed polymerizations by reversing the addition order of the two bases. TMPIP or DMDPS was added first before the start of polymerization, followed by the addition of TBME with 5- or 10-min delay. The kinetic curves are plotted in Figures 3 and 4, and the polymerization results are tabulated in Table IV. There was a noticeable enhancement of polymerization rate after the introduction of TBME, but the overall rates were substantially lower than the case where TBME was added first. The result led us to believe that the small

enhancement of the polymerization rate could be due to additional site activation by TBME, but the large majority of sites already coordinated with TMPIP or DMDPS could not be affected by the



**Figure 3** Kinetic curves of propene polymerization with catalyst A. Polymerization conditions were the same as in Table IV: ( $\bullet$ ) TMPIP (TMPIP/TEA = 0.05); ( $\circ$ ) TMPIP+TBME (TMPIP/TEA = 0.05, TBME/TEA = 0.029) where TBME was added 5 min after the start of polymerization.

**Table IV** Effects of External Base Pairs on Propene Polymerization. Polymerization Conditions Were the Same as in Table 1. The Addition Order of the Two External Bases Was TMP/IP or DMDPS First, Followed by TBME With a Specified Time Delay.

Catalyst	External Base Pair <sup>a</sup>	Time of TBME Addition (min)	Activity (kg PP/g Ti/h)	I.I. <sup>b</sup> (wt %)	[mm] <sup>c</sup> (mol %)
A	TMPIP, TBME	5	9.9	96.4	95.4
	DMDPS, TBME	10	9.0	96.5	95.7

<sup>a</sup> TMP/IP or DMDPS/TEA = 0.05 and TBME/TEA = 0.029.

<sup>b</sup> I.I. = isotactic index measured as the weight percent of polymer insoluble in boiling heptane.

<sup>c</sup> [mm] = isotactic triad of isotactic polymer estimated from IR spectrum.

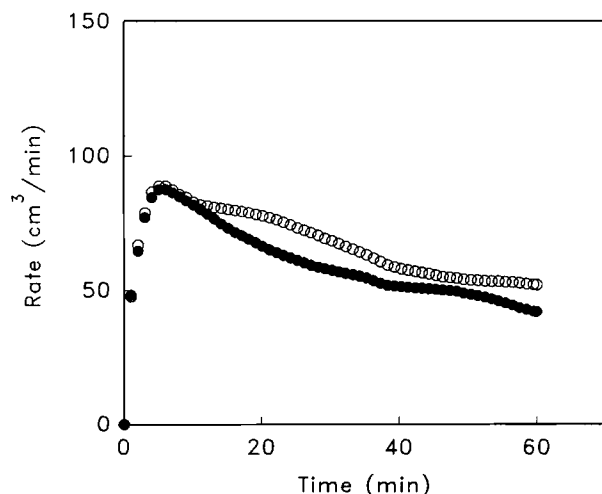
subsequent addition of TBME, resulting in an overall rate reduction. I.I. of the whole polymers and [mm] of the isotactic polymers also support the above explanation.

In conclusion, we have shown that the role of TBME is somewhat different from TMP/IP or DMDPS in the propene polymerization with MgCl<sub>2</sub>/DOP/TiCl<sub>4</sub>-TEA catalyst. By pairing two external bases of different types, TBME with TMP/IP or DMDPS with TBME added first, followed by the other, an improvement of catalyst activity as well as isotacticity was observed.

## Experimental

A detailed description for the preparation of catalysts A, B, and C and polymerization procedure is given elsewhere.<sup>7,8</sup> The loadings of titanium, DOP,

and POC in catalyst were also reported. The isotactic index (I.I.) of polypropene was determined as the percent of polymer insoluble in boiling heptane after 12 h in a soxhlet extractor. The experimental error was estimated by replications to be  $\pm 1.1\%$  of standard deviation. The estimation was based on two or three replications of 12 different samples. The isotactic triad, [mm], of the isotactic portion of the polymer was evaluated from the IR spectrum of the isotactic polymer as recommended by Burfield and Loi.<sup>21</sup> For IR measurements, polymer films were prepared by hot pressing about 50 mg of polymer between aluminum foil at 200°C. The spectrum was obtained by using a Bomem MB120 FTIR. The confidence interval for [mm] measurement was calculated to be  $\pm 0.3$  mol % without considering the inherent precision of the FTIR. The estimation was made from three measurements of ten different samples.



**Figure 4** Kinetic curves of propene polymerization with catalyst A. Polymerization conditions were the same as in Table IV: (●) DMDPS (DMDPS/TEA = 0.05); (○) DMDPS+TBME (DMDPS/TEA = 0.05, TBME/TEA = 0.029) where TBME was added 10 min after the start of polymerization.

## REFERENCES

1. P. C. Barbe, G. Cecchin, and L. Noristi, *Adv. Polym. Sci.*, **81**, 1 (1987).
2. K. Soga, T. Shiono, and Y. Doi, *Makromol. Chem.*, **184**, 1531 (1988).
3. A. Proto, L. Oliva, C. Pellicchina, A. J. Sivak, and L. A. Callo, *Macromolecules*, **23**, 2904 (1990).
4. R. Spitz, C. Bobichon, and A. Guyot, *Makromol. Chem.*, **190**, 707 (1989).
5. J. C. W. Chien and Y. Hu, *J. Polym. Sci.: Poly. Chem. Ed.*, **26**, 2973 (1988).
6. C. B. Yang, C. C. Hsu, Y. S. Park, and H. F. Shurvell, *Eur. Polym. J.*, **30**, 205 (1994).
7. C. B. Yang and C. C. Hsu, *Polym. Bull.*, **30**, 529 (1993).
8. C. B. Yang and C. C. Hsu, *Makromol. Chem. Rapid Commun.*, **14**, 387 (1993).
9. A. W. Langer, T. J. Burkhardt, and J. J. Steger, *Polym. Sci. Technol.*, **19**, 225 (1983).
10. P. Galli, L. Luciani, and G. Cecchin, *Angew. Makromol. Chem.*, **94**, 63 (1984).

11. V. Busico, P. Corradini, L. De Martino, A. Proto, and V. Savino, *Makromol. Chem.*, **186**, 1279 (1985).
12. K. Soga and T. Shiono, *Transition Metal Catalyzed Polymerization, Ziegler-Natta and Metathesis Polymerization*, R. P. Quirk, Ed., Cambridge University Press, New York, 1988, p. 266.
13. N. Kashiwa, M. Kawasaki, and J. Yoshitake, *Studies in Surface Science and Catalysis*, vol. 25, T. Keii and K. Soga, Eds., Elsevier, Tokyo, 1986, p. 43.
14. N. Kashiwa, J. Yoshitake, and A. Toyota, *Polym. Bull.*, **19**, 333 (1988).
15. N. Kashiwa, J. Yoshitake, and T. Tsutsui, *Polym. Bull.*, **19**, 339 (1988).
16. R. Ohnishi, H. Funabashi, and A. Tanaka, *Makromol. Chem. Rapid Commun.*, **12**, 19 (1991).
17. M. Kakuko, T. Miyatake, Y. Naito, and K. Mizunuma, *Macromolecules*, **21**, 314 (1988).
18. C. Dumas, Ph.D. Thesis, Queen's University, Kingston, Ontario, Canada, 1985.
19. Y. Doi, M. Murata, and K. Yano, *Ind. Eng. Chem. Prod. Res. Dev.*, **21**, 580 (1982).
20. U. Giannini, *Makromol. Chem. Suppl.*, **5**, 216 (1981).
21. D. R. Burfield and P. S. T. Loi, *J. Appl. Polym. Sci.*, **36**, 279 (1988).

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